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The effect of ligands, solvent and temperature on the reactions of allyltin(IV) compounds with singlet oxygen

H.-S. Dang [1] and A.G. Davies
Chemistry Department, University College London, 20 Gordon Street, London, WC1H 0AJ (UK)

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Abstract

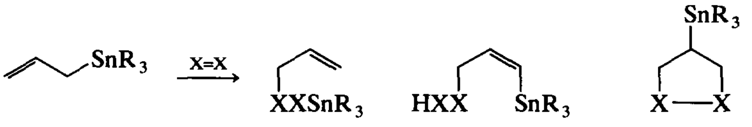
The reaction of singlet oxygen with a variety of allyltin compounds $CH_2{=}CHCH_2SnR_3$ (R_3 = Me_3, Bu_3, allyl$_3$, (cyclo-C_6H_{11})$_3$, Ph_3, allylBu$_2$, Bu_2Cl, Bu_2OAc, allylCl$_2$, allylCl$_2$bipy) has been investigated, and the allylperoxytin compounds, 3-stannylallyl hydroperoxides, and 4-stannyl-1,2-dioxolanes which result from M-ene, H-ene and cycloaddition processes, respectively, have been identified by NMR spectroscopy. As the tin centre becomes more electropositive, as indicated by the ^{13}C NMR shift of the allylic CH_2 group, the proportion of the M-ene reaction increases, and when δCH_2 is above about 23.7, the allylperoxytin compound is the only product. An exception to this rule is tetraallyltin, δCH_2 16.13, which similarly shows only the M-ene reaction. This is tentatively ascribed to the special effect of hyperconjugation between the C–Sn σ-bond and the remaining π-systems.

A polar solvent favours the M-ene reaction. The cycloaddition reaction is favoured by low temperature, and at −70°C in a non-polar solvent it may become the major route.

Diallylmercury and allylmercury chloride react with singlet oxygen to show only the M-ene reaction, but also undergo extensive photosensitized decomposition. With 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), allylmercury chloride shows only the M-ene reaction.

Introduction

Allylic tin compounds react with singlet oxygen or with PTAD to give the products of M-ene (**1**), H-ene (**2**) and cycloaddition (**3**) reactions as shown in eq. 1, in relative yields which depend on the structural and environmental conditions [1,2].



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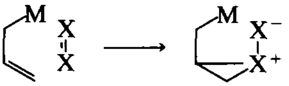
1 M-ene **2** H-ene **3** Cycloaddition

Correspondence to: Professor A.G. Davies, Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, UK.

[1] Present address: Chemistry Department, Lanzhou University, Lanzhou, People's Rep. of China.

These reactions show none of the characteristics of radical chain reactions, and it seems likely that the mechanism of the M-ene reaction and the cycloaddition reactions are related to that of the H-ene reactions of allylic hydrocarbons [1]. A reasonable model is that they involve the prior formation of a complex between the ene and the eneophile (X=X) which may be represented as a perepoxide when $^1O_2$ reacts, or an aziridineimine when PTAD is the reagent (eq. 2). Pericyclic transfer of the metal (eq. 3) or of hydrogen (eq. 4) may then lead to the M-ene and H-ene products respectively, and the cyclization with migration of the metal may be a consequence of the familiar β-effect of an organometallic group which stabilises a carbonium ion by forming a bridged intermediate (eq. 5) [2].



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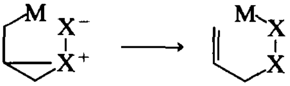

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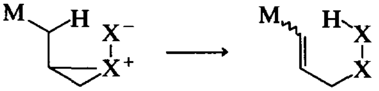

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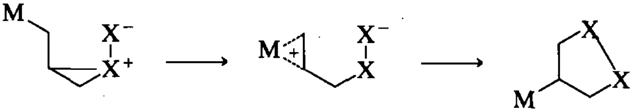

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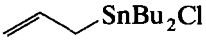
We were interested in investigating the effect on these three reaction routes of the nature of the ligands about the tin centre, the polarity of the solvent, and the temperature: if the reactions could be made more selective they would be more useful in organic synthesis, and knowledge of the factors which affect the rates of the three processes might provide information on the vexed question of the mechanism of the H-ene reactions. We report here a study of the reaction of singlet oxygen and of PTAD with allyldibutyltin chloride (**4**), diallyltin dichloride (**5**), allyltrimethyltin (**6**), allyltributyltin (**7**), diallyldibutyltin (**8**), allyltriphenyltin (**9**), allyltricyclohexyltin (**10**), allyldibutyltin acetate (**11**), bipyridyldiallyltin dichloride (**12**) and tetraallyltin (**13**). The behaviour of diallylmercury and allylmercury chloride has also been briefly investigated.



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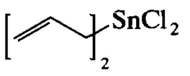

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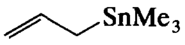

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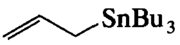

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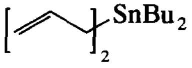

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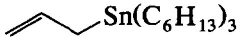

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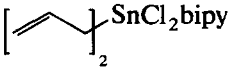

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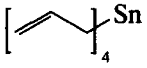


(13)

Results

The allyltin compounds **6–10** were prepared by a modified Grignard procedure in which a solution of the trialkyltin chloride and a 5-fold excess of allyl bromide in ether or THF was added to a 5-fold excess of magnesium. Tetraallyltin (**13**) was obtained by treating tin tetrachloride with allylmagnesium bromide which was prepared from magnesium which was activated by dry stirring [3]. Compounds **4**, **5**, **11** and **12** were prepared by standard methods. In a quest for some correlation between NMR chemical shifts or coupling constants as a measure of electronegativity, and chemoselectivity, the ^{119}Sn and ^{13}C NMR spectra of the allytin(IV) compounds **4–12** were recorded, and the results are summarised in Table 1.

We have shown previously that with $^1O_2$ as the eneophile, the M-ene products **1** are converted into the corresponding hydroperoxides during chromatography on silica gel, and the H-ene products **2** and the cyclization products **3** decompose [2]. No attempts have therefore been made to isolate these compounds, and they have instead been identified by high resolution ^{1}H NMR spectroscopy on the basis of the data reported in Ref. 2.

The products which were obtained when the allyltin compounds **4–13** were allowed to react with singlet oxygen which was generated photochemically using tetraphenylporphine (TPP) as a sensitizer are shown in Table 2.

Addition of pyridine to **4** did not affect the course of the reaction. No added sensitizer was necessary in the reaction of the 6-coordinate bipyridyl complex **12**:

Table 1

^{119}Sn and ^{13}C NMR spectra of allyltin compounds [a]

	Allyltin compound									
	4	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
δ(^{119}Sn)	+132.5	+82.0	−4.6	−18.2	−26.1	−122.0	−77.9	−148.8	−324.0	
δ(C-1)	23.68	30.23	18.05	16.16	16.21	17.80	14.11	24.85	48.6	16.13
J(^{117}Sn)	(270.5)	(381.5)	(283.1)	(233.8)	(240.7)	(325.8)	(197.5)	(291.7)	(926.2)	(252.6)
J(^{119}Sn)	(282.5)	(398.7)	(296.1)	(244.6)	(251.9)	(340.5)	(206.5)	(305.2)	(969.3)	(263.6)
δ(C-2)	134.1	129.9	137.6	138.16	137.6	135.80	138.8	134.9	135.7	136.56
J(Sn)	(59.4)	(76.5)	(47.2)	(40.6)	(43.0)	(43.8)	(39.8)	(49.3)	(117.4)	
δ(C-3)	113.3	117.9	109.4	109.1	109.8	112.3	109.3	112.5	113.0	111.07
J(Sn)	(62.6)	(72.5)	(49.1)	(42.5)	(45.8)	(52.4)	(41.6)	(51.5)	(142.6)	
δ(C-other)	13.57		−10.35	9.10	9.40	138.34	26.7	13.62	121.3(2C)	
	17.43		(314.2)	(304.5)	(308.3)	(473.9)	(307.4)	16.57	126.3	
	(328.1)		(328.3)	(318.4)	(322.8)	(495.6)	(321.8)	26.98	140.4	
	(342.5)			13.69	13.68	137.05	27.2	27.73	148.7(2C)	
	26.78			27.31	27.22	(35.1)	(3.5)	26.61		
	27.73			(52.5)	(53.7)	129.0	29.3	148.1		
				29.10	28.94	(12.5)	(52.3)			
				(20.4)	(21.3)	128.50	32.3			
						(49.4)	(16.7)			

[a] When they are not labelled, $^{117/119}$Sn coupling constants are enclosed in parentheses below the δ value for the signal. When two values are given the first refers to J(^{117}Sn) and the second to J(^{119}Sn); when only one value is given it refers to an average value of J(^{117}Sn) and J(^{119}Sn), which were unresolved.

Table 2

Products from the reaction of allyltin compounds with singlet oxygen

Reactant		Products (%)					
	R_3 =	**1**		**2**		**3**	
4	Bu_2Cl	**14**	100	–		–	
5	allylCl_2	**15**	100	–		–	
6	Me_3	**16**	25	**17**	50	**18**	25
7	Bu_3	**19**	18	**20**	40	**21**	42
8	allylBu_2	**22** [a]	62	**23**	28	**24**	10
9	Ph_3	**25**	42	**26**	53	**27**	5
10	$(c\text{-}C_6H_{11})_3$	**28**	< 5	**29**	37	**30**	58
11	Bu_2OAc	**31**	100	–		–	
12	allylCl_2bipy	**32** [a]	100	–		–	
13	$(allyl)_3$	**33** [b]	100	–		–	

[a] Two allyl groups reacted to give products $(allylO_2)_2SnR_2$. [b] Four allyl groups reacted to give $(allylO_2)_4Sn$.

although the ligand and the complex are not noticeably coloured the compound can act as its own sensitizer towards sodium light.

We hoped to test further the importance of the coordination state of the tin by studying the reaction with allylstannatrane, CH_2=$CHCH_2Sn(OCH_2CH_2)_3N$, which would be expected to be strongly 5-coordinated, but despite a number of attempts we were unable to prepare a pure sample of the compound.

Tetraallyltin (**13**) reacted with 4 equivalents of $^1O_2$ to give only the product of four sequential M-ene reactions (eq. 6).

$$(CH_2{=}CHCH_2)_4Sn + 4\ O_2 \longrightarrow (CH_2{=}CHCH_2OO)_4Sn \qquad (6)$$

The reaction of dibutyldiallyltin (**8**) is more complicated in that all three possible types of reaction take place, and the groups which are formed could in principle be combined in six ways to give six products. Only one example of each group could be detected in the ^1H NMR spectrum and for simplicity we have assumed in Table 2 that only symmetrical combinations of the three groups are present, though it is more likely that all combinations are present but different ones cannot be distinguished.

The effect of solvent and of temperature on the reaction of allyltricyclohexyltin (**10**) with singlet oxygen was investigated briefly, and compared with the reactions using PTAD as the enophile. The results are shown in Table 3.

Table 3

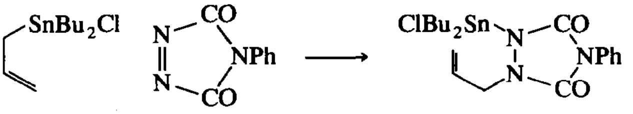
The effect of solvent and of temperature on the reaction of **10** with $^1O_2$ and with PTAD

T (°C)	Solvent	Yield (%)					
		X=X = $^1O_2$			X=X = PTAD		
		28	**29**	**30**	**31**	**32**	**33**
20	$CHCl_3$	< 5	37	58	63	0	37
−70	CD_2Cl_2	< 5	20	75	–	–	–
15	$CDCl_3/CD_3CN$	22	45	33	80	0	20

Change of the solvent from $CDCl_3$ to a mixture of $CDCl_3$ and CD_3CN (2/3 v/v) caused an increase in the yield of the H-ene product **29** and particularly of the M-ene product **28** at the expense of the dioxolan **30**. Similarly in the reaction with PTAD the more polar solvent favoured the production of the M-ene product **34**. We observed a similar effect previously in the reaction of cyclohex-2-enyltributyltin with singlet oxygen, and of allyltrimethyltin with PTAD in CH_2Cl_2 and in methanol/benzene mixture [2].

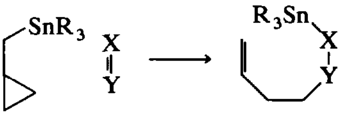
Reduction of the temperature of the reaction of **10** with singlet oxygen favoured the cycloaddition reaction, and we obtained the highest yield of the 4-stannyldioxolane **30** (75%) by carrying out the reaction at $-70°C$ in CD_2Cl_2.

Our previous work has emphasised the parallel between the behaviour of singlet oxygen and of PTAD as an enophile [1,2], and we had showed that allyltributyltin reacted with PTAD to give the products of M-ene, H-ene, and cycloaddition reactions in yields of 5, 25 and 70%, respectively. We have now carried out the reaction of PTAD with **4** at 20°C, and find that the parallel with $^1O_2$ persists, and the reaction now gives exclusively the M-ene product (eq. 7).



(7)

A cyclopropyl group often shows some characteristics of unsaturation. Cyclopropylmethyltrimethyltin reacts with SO_2 by what appears to be an M-ene reaction (eq. 8, X=Y = O=SO) [4], and it seemed possible that a cyclopropylmethyltin compound might show M-ene reactivity towards singlet oxygen or PTAD (eq. 8, X=Y = RN=NR or O=O). However we could observe no reaction between cyclopropylmethyltrimethyltin and singlet oxygen or PTAD over a long period.



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The reaction of two allylmercury compounds was investigated briefly. When diallylmercury or allylmercury chloride in $CDCl_3$ in the presence of TPP and oxygen was irradiated with sodium light, mercury and mercury oxide separated and the principal product was acrolein together with some of the M-ene product (eq. 9). Presumably the acrolein is derived from oxidation of the propenyl radical which results from photosensitized homolysis of the allylmercury.

$$(CH_2{=}CHCH_2)_2Hg + {}^1O_2 \xrightarrow{h\nu} Hg + CH_2{=}CHCH{=}O + Hg(OOCH_2CH{=}CH_2)_2 \quad (9)$$

To avoid this complication of homolysis of the allylmercury compound, allylmercury chloride was treated with PTAD in $CDCl_3$. The only product which was detected was that of the M-ene reaction (eq. 10), and no hydrogen shift or cycloaddition was observed.

$$CH_2{=}CHCH_2HgCl + PTAD \longrightarrow CH_2{=}CHCH_2(PTAD)HgCl \quad (10)$$

Discussion

The most obvious feature of the entries in Table 2 is that allyltin compounds which carry an electronegative ligand (Cl or OAc) on the tin (compounds **4**, **5**, **11**) react with singlet oxygen to give the products **1** of the M-ene reaction in quantitative yield. It appears that the reaction is favoured by a more electropositive tin centre.

The effect of varying the organic ligands R in the reaction with $R_3SnCH_2CH=CH_2$ with singlet oxygen is illustrated by compounds **6–10** in Table 1. As R is changed from methyl to butyl and then to cyclohexyl (compounds **6**, **7** and **10**), the product of cycloaddition is favoured at the expense of the M-ene and H-ene reactions. This might be a consequence of increased electron release from the groups R and/or from their increasing steric effect, both of which might reduce the coordination of oxygen to tin in the intermediate **1**, which we think favours the M-ene reaction. In accord with this, the triphenylstannyl group in **9**, which would be coordinated more strongly than a trialkyltin group, leads to the formation of more of the M-ene product **25**.

No correlation is apparent between the chemoselectivity and the ^{119}Sn NMR chemical shift of the substrate; this is hardly surprising as $\delta(^{119}Sn)$ is dominated by the paramagnetic term, and is not suitable as a measure of electronegativity [5]. On the other hand, within the limitation of the few compounds which we have yet studied, the value of $\delta(^{13}C)$ for the allylic methylene group does appear to give some guide to chemoselectivity. The four compounds with $\delta(^{13}C)$ 23.68 or greater give only the M-ene product with singlet oxygen or PTAD in $CDCl_3$, whereas the other compounds with $\delta(^{13}C)$ 18.05 or less (with the exception of tetrallyltin) give also the H-ene and cycloaddition products. Within this latter family, as the value of $\delta(CH_2)$ decreases in the allyltrialkyltins **6**, **7** and **10**, the yield of the M-ene product decreases in the same sequence.

Within a closely related family of compounds, the values of $\delta(^{13}C_\alpha)$ of a constant reference group, here allyl, do reflect the electronegativity at the tin, and our belief is strengthened that the M-ene process is favoured by an electropositive tin centre. This might act by establishing intramolecular coordination of oxygen to the metal in the perepoxide or aziridinium imide intermediate.

In an attempt to identify this assumed perepoxide intermediate containing 5-coordinate tin, the reaction of **4** with singlet oxygen was carried out at −70°C, and the ^{1}H NMR spectrum was immediately recorded at this temperature, but no signals other than those relating to **14** could be detected.

If the course of the reaction is determined in part by coordination of the eneophile to the metal in the reaction intermediate, the nature of the products might be expected to be affected by the state of the coordination of the substrate. It was in order to investigate this that we examined the reaction of allyldibutyltin chloride (**4**) in the presence of pyridine, and of the 6-coordinate bipyridyl complex (**12**) of diallyltin dichloride, but both reactions still showed only the M-ene reaction. It appears that either coordination of the eneophile to the tin is not important in inducing the M-ene reaction, or that oxygen of the perepoxide can effectively compete intramolecularly with the intermolecular coordination by the nitrogen.

Comparison of the behaviour of compounds **7**, **8** and **13** suggests that the

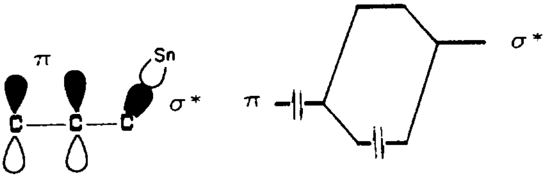
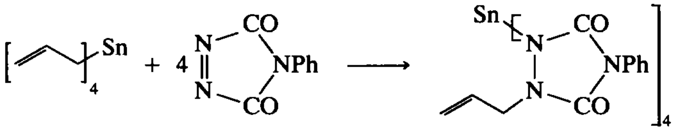


Fig. 1. $\sigma^*-\pi$ conjugation in allyltin compounds.

presence of two or more allyl groups encourages the first to undergo the M-ene reaction rather than the H-ene reaction or cycloaddition, and indeed tetraallyltin reacted cleanly with PTAD to give only the M-ene product **34** (eq. 11) although the value of $\delta(CH_2)$ is 16.13.



(11)

We suggest that this interesting behaviour may result from $\pi-\sigma^*$ conjugation between the C=C double bonds and the CH_2–Sn bonds of the allyl groups which are not involved in the M-ene reaction (Fig. 1). In the ground state this effect causes the CH_2–Sn bond to lie orthogonal to the plane of the π-system [6] and it may be called more into play in the transition state.

We thought that, in view of the propensity of mercury to form mercurinium ions, allylmercury compounds might react with singlet oxygen to give by reaction 5 a substantial amount of 4-mercuri-1,2-dioxolans, which have been prepared previously from the ring-closure of allyl hydroperoxides in the presence of mercury(II) salts [7–11]. Allylmercury chloride however reacted with singlet oxygen to give only the open-chain peroxide.

Low temperatures and non-polar solvents appear to be conducive to reaction 5, but the maximum yield of dioxolane that we have yet achieved is 75%.

Conclusion

These results have established that with sufficiently electropositive tin groups, as measured by the ^{13}C NMR shift of the α-CH_2 group, allyltin compounds can react with singlet oxygen to give quantitative yields of the M-ene products. With less electronegative ligands on the tin, and in a non-polar solvent at low temperature, yields of up to 75% of the 4-stannyl-1,2-dioxolanes can be obtained.

Experimental

The ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded in $CDCl_3$ on a Varian VXR-400 spectrometer. ^1H and ^{13}C chemical shifts were referenced to the solvent (δ(H) 7.24, δ(C) 77.00), and ^{119}Sn chemical shifts to Me_4Sn (0.00 ppm). Coupling constants are in Hz.

Allyldibutyltin chloride (4)

This was prepared by Tagliavini's method [12]. B.p. 105°C/1 mmHg (ref. 12: 97–98°C/0.5 mmHg). δ(H) 0.90 (t, 6H, *J* 7.33, CH_3); 1.34 (m, 8H, CH_2CH_2); 1.63 (m, 4H, CH_2); 2.19 (dm, 2H, *J* 8.45 and 1.70, $J(^{119}Sn)$ 69.36, $J(^{117}Sn)$ 66.34, H-1); 4.85 (dm, 1H, *J* 10.08 and 2.15, *E*-H-3); 4.96 (dm, 1H, *J* 16.88 and 1.15 *Z*-H-3); 5.93 (ddt, 1H, *J* 16.90, 10.05 and 8.45, H-2).

Diallyltin dichloride (5)

This was prepared by distilling a mixture of equivalent amounts of tetraallyltin and tin tetrachloride [13]. B.p. 68°C/0.5 mmHg. δ(H) 2.69 (dm, 4H, *J* 8.17 and 1.12, $J(^{119}Sn)$ 82.76, $J(^{117}Sn)$ 79.10, H-1); 5.11 (dm, 2H, *J* 10.04 and 2.15, *E*-H-3); 5.19 (dm, 2H, *J* 16.91 and 1.31, *Z*-H-3); 5.93 (ddt, 2H, *J* 16.90, 10.05 and 8.20, H-2).

Compounds **6–10** were prepared by a modified Grignard method [2] in which a solution of the trialkyltin chloride and allyl bromide (5 mol equiv.) in ether (for compounds **6**, **7** and **8**) or tetrahydrofuran (for compounds **9** and **10**) was added to magnesium (equivalent to the allyl bromide) with vigorous stirring under argon at such a rate to maintain gentle refluxing. (This method was particularly useful for preparing compound **10**, where the usual Grignard procedure gave mainly hexabutylditin). After working up the reaction mixture, the products were chromatographed on silica gel using pentane as eluent, to give compounds **6–10** in 85–95% yield.

Allyltributyltin (7)

B.p. 90°C/0.4 mmHg (ref. 14: 94–95°C/0.55 mmHg). δ(H) 0.91 (m, 15H, CH_2CH_3); 1.30 (m, 6H, CH_2); 1.50 (m, 6H, CH_2); 1.75 (dm, 2H, *J* 8.70 and 0.90, $J(^{119}Sn)$ 51.45, $J(^{117}Sn)$ 49.20, H-1); 4.26 (dm, 1H, *J* 10.02 and 2.19, *E*-H-3); 4.76 (dm, 1H, *J* 16.81 and 0.95, *Z*-H-3); 5.92 (ddt, 1H, *J* 16.81, 10.02 and 8.70, H-2).

Diallyldibutyltin (8)

B.p. 122–125°C/0.5 mmHg (ref. 15: 93°C/0.1 mmHg). δ(H) 0.87 (t, 6H, *J* 7.85); 0.91 (t, 4H, *J* 7.86, CH_2); 1.26 (m, 8H, CH_2CH_2); 1.48 (m, 4H, CH_2); 1.80 (dm, 4H, *J* 8.43 and 1.07, $J(^{119}Sn)$ 61.9, $J(^{117}Sn)$ 59.2, H-1); 4.66 (dm, 2H, *J* 10.01 and 2.09, *E*-H-3); 4.79 (dm, 2H, *J* 16.85 and 1.05, *Z*-H-3); 5.91 (2H, ddt, *J* 16.85, 10.01 and 8.43, H-2).

Allyltriphenyltin (9)

M.p. 75°C (ref. 13: 72–74°C). δ(H) 2.45 (d, 2H, *J* 8.39, $J(^{119}Sn)$ 72.94, $J(^{117}Sn)$ 69.75, H-1); 4.80 (dm, 1H, *J* 10.89 and 2.05, *E*-H-3); 4.97 (dm, 1H, *J* 16.85 and 1.47, *Z*-H-3); 6.07 (ddt, 1H, *J* 16.85, 10.88, and 8.40, H-2); 7.39 (m, 9H, ArH); 7.55 (m, 6H, ArH).

Allyltricyclohexyltin (10)

Viscous oil. δ(H) 1.25 (m, 6H); 1.52 (m, 6H); 1.65 (m, 6H); 1.76 (dm, 2H, *J* 8.64 and 0.75, H-1; the tin satellites overlap the signals of the ring protons); 1.83 (m, 4H); 4.63 (dm, 1H, *J* 16.85 and 1.05, *E*-H-3); 5.98 (ddt, 1H, *J* 16.85, 9.82 and 8.65, H-2). Values of δ(C) are given in Table 1. ν_{max} (neat) 2953, 2918, 2846, 1458, 1376, 1072, 876 cm^{-1}. Found: C, 59.45; H, 9.85. $C_{19}H_{38}Sn$ calc.: C, 59.24; H, 9.94%.

Allyldibutyltin acetate (11)

The chloride **4** was hydrolysed with aqueous KOH to the corresponding hydroxide. This was warmed with acetic acid and the product was purified by chromatography on silica gel with pentane/CH_2Cl_2 (10/1 v/v) as eluent, giving **11** (70% yield), m.p. 55°C, b.p. 75°C/ 1 mmHg (ref. 16: 127°C/10 mmHg). δ(H) 0.90 (t, 6H, *J* 7.20, CH_3); 1.32 (complex, 8H, CH_2); 1.61 (m, 4H, CH_2); 2.03 (s, 3H, $CH_3C{=}O$); 2.12 (d, 2H, *J* 8.58, *J*(Sn) 68.62, H-1); 4.79 (dm, 1H, *J* 9.99 and 1.78, *E*-H-3); 4.91 (dm, 1H, *J* 16.88 and 1.65, *Z*-H-3); 5.94 (ddt, 1H, *J* 16.90, 10.01, and 8.60, H_2). Values of δ(C) are given in Table 2.

Bipyridyldiallyltin dichloride (12)

The complex was obtained as white needles, m.p. 194–196°C, in 65% yield from the reaction of diallyltin dichloride and bipyridyl in THF. δ(H) 2.51 (d, 4H, *J* 8.49, $J(^{119}Sn)$ 153.04, $J(^{117}Sn)$ 146.25, H-1); 4.08 (dm, 2H, *J* 18.50 and 1.07, *E*-H-3); 4.12 (dm, 2H, *J* 10.05 and 2.05, *Z*-H-3); 5.52 (ddt, 2H, *J* 18.50, 10.05 and 8.50, H-2); 7.71 (brt, 2H, *J* 6.03); 8.16 (brt, 2H, *J* 8.07); 8.23 (brd, 4H, *J* 8.05); 9.41 (brd, 2H, *J* 3.60). Values of δ(C) are given in Table 1. Found: C, 44.85; H, 4.15; N, 6.4. $C_{16}H_{18}Cl_2N_2Sn$ calc.: C, 44.91; H, 4.24; H, 6.55%.

Tetra-allyltin (13) [17]

This was prepared by the reaction between tin tetrachloride and allylmagnesium bromide, which was obtained from magnesium activated by Brown's method [3]. δ(H) 1.90 (dt, 8H, *J* 8.58 and 0.69, $J(^{117}Sn)$ 61.40, $J(^{119}Sn)$ 64.24, CH_2); 4.73 (dm, 4H, *J* 10.05 and 1.15); 4.85 (dm, 4H, *J* 16.87 and 0.50); 5.91 (ddt, 4H, *J* 16.87, 10.05 and 8.58). δ(C) 16.13 ($J(^{117}Sn)$ 252.6, $J(^{119}Sn)$ 263.6); 111.07; 136.56.

Cyclopropyltrimethyltin [18]

δ(H) −0.03 (m, 2H) 0.06 (s, 9H, $J(^{119}Sn)$ 52.8, $J(^{117}Sn)$ 50.5, Me); 0.44 (m, 2H); 0.77 (m, 3H, $CHCH_2Sn$). δ(C) −10.06; 7.75; 8.93; 16.9.

Diallylmercury [19]

δ(H) 1.90 (d, 4H, *J* 7.94, $J(^{199}Hg)$ 144.5); 4.61 (dm, 2H, *J* 9.85 and 2.17, *E*-H-3); 4.72 (dm, 2H, *J* 16.51 and 1.92); 6.01 (ddt, 2H, *J* 16.51, 9.85 and 7.95, *Z*-H-3).

Allylmercury chloride [19]

M.p. 110°C (ref. 19: 111°C). δ(H) 2.77 (d, 2H, *J* 8.25, $J(^{199}Hg)$ 260.9, H-1); 4.94 (dm, 1H, *J* 9.85 and 0.95, *E*-H-3); 5.07 (dm, 1H, *J* 16.68 and 1.27, *Z*-H-3); 5.97 (ddt, 1H, *J* 16.70, 9.90 and 8.25, H-2).

Photooxygenation

Photooxygenation was carried out with a sodium lamp and tetraphenylporphine (TPP; in non-polar solvents) or Rose Bengal (in polar solvents) as reported previously [2]. Reactions were also carried out in an NMR tube, with oxygen bubbling through the solution.

The allylperoxytin compounds produced by M-ene reactions were converted to allyl hydroperoxide during chromatography on silica gel; this was reduced by triphenylphosphine to allyl alcohol, and identified by NMR. The stannyldihydropyrazoles were similarly converted to the dihydropyrazoles, which were separated and identified [2]. Products from the H-ene and cycloaddition reactions of singlet oxygen decomposed on silica gel, and were identified in the reaction mixture by high resolution NMR.

Characteristics of the products were as follows.

Allylperoxychlorodibutyltin (14). δ(H) 0.90 (t, 6H, *J* 7.45); 1.37 (m, 4H, CH_2); 1.75 (m, 8H, CH_2CH_2); 4.50 (d, 2H, *J* 6.40, CH_2O); 5.52 (dm, 1H, *J* 10.10 and 2.25, *E*-H-3); 5.30 (dm, 1H, *J* 17.19 and 1.27); 5.89 (ddt, 1H, *J* 17.20, 10.10, and 6.40, *Z*-H-3); δ(C) 13.65; 26.35; 26.42 and 26.76 (Bu); 82.51 (CH_2); 121.50 and 135.04 (C=C). **14** was similarly formed when **4** was treated with $^1O_2$ in the presence of pyridine.

1-Allyl-2-dibutylchlorostannyl-4-phenyl-1,2-dihydrotriazolinedione. δ(H) 0.89 (t, 6H, *J* 7.46); 1.35 (m, 4H); 1.80 (m, 8H); 4.22 (d, 2H, *J* 5.83); 5.20 (dm, 1H, *J* 9.51 and 2.18); 5.24 (dm, 1H, *J* 16.34 and 1.27); 5.82 (ddt, 1H, *J* 16.35, 9.55 and 5.83); 7.35–7.50 (5H, complex). δ(C) 13.48; 26.26 (2C); 26.76; 47.91; 118.81 and 132.02 (2 vinyl carbons); 125.49; 127.81; 128.90 and 131.66 (4 aromatic carbons); 151.83 and 153.20 (C=O).

Diallylperoxydichlorotin (15). δ(H) 4.50 (d, 2H, *J* 6.18, CH_2O); 5.33 (dm, 1H, *J* 10.33 and 2.28, *E*-H-3); 5.37 (dm, 1H, *J* 17.16 and 1.34, *Z*-H-3); 6.00 (ddt, 1H, *J* 17.15, 10.30 and 6.15, H-2).

The products **16**, **17** and **18** were identified previously [2], and with that information the remainder of the M-ene, H-ene, and cyclic products could be identified as follows.

Allylperoxytributyltin (19). δ(H) 4.44 (d, 2H, *J* 6.48, CH_2O); 5.30 (dm, 1H, *J* 10.73 and 2.25, *E*-H-3); 5.35 (dm, 1H, *J* 17.28 and 1.28, *Z*-H-3); 5.94 (ddt, 1H, *J* 17.28, 10.70 and 6.46, H-2).

3-(Tributylstannyl)allyl hydroperoxide (20). δ(H) 4.48 (d, 2H, *J* 6.45, CH_2); 6.27 (d, 1H, *J* 12.98, *J*(Sn) 75.5, H-1); 6.63 (dt, H, *J* 12.98 and 6.46, *J*(Sn) 141.5, H-2).

4-Tributylstannyl-1,2-dioxolane (21). δ(H) 2.29 (tt, 1H, *J* 11.45 and 7.98, H-4); 3.81 (dd, 2H, *J* 11.45 and 6.83, *E*-H-3,5); 4.31 (dd, 2H, *J* 7.98 and 6.83, *Z*-H-3,5).

Diallylperoxydibutyltin (22). δ(H) 4.42 (d, 4H, *J* 10.39 and 2.15, CH_2O); 5.32 (dm, 1H, *J* 17.19 and 1.25, *Z*-H-3); 5.91 (ddt, 2H, *J* 17.20, 10.35 and 6.45, H-2).

Dibutyldi(3-hydroperoxyprop-1-enyl)tin (23). δ(H) 4.42 (d, 4H, *J* 6.48, CH_2); 6.25 (d, 1H, *J* 13.54, *J*(Sn) 78.8, H-1); 6.64 (dt, 1H, *J* 13.55 and 6.48. *J*(Sn) 152.4, H-2).

Dibutyldi(1,2-dioxolan-4-yl)tin (24). δ(H) 2.34 (tt, 2H, *J* 11.29 and 8.08, H-4); 3.83 (dd, 4H, *J* 11.28 and 6.70, *E*-H-3,5); 4.31 (dd, 4H, *J* 8.08 and 6.70, *Z*-3,5).

Allylperoxytriphenyltin (25). δ(H) 4.46 (br d, 2H, *J* 6.24, CH_2O); 5.33 (dm, 1H, *J* 10.17 and 2.45, *E*-H-3); 5.38 (dm, 1H, *J* 17.22 and 1.05); 5.96 (ddt, 1H, *J* 17.22, 10.18 and 6.25, H-2).

3-(Triphenylstannyl)allyl hydroperoxide (26). δ(H) 4.49 (d, 2H, *J* 5.52, CH_2O); 6.27 (d, 1H, *J* 12.91, *J*(Sn) 78.5, H-1); 6.92 (dt, 1H, *J* 12.91 and 5.56, *J*(Sn) 165.2, H-2).

4-Triphenylstannyl-1,2-dioxolane (27). δ(H) 2.94 (tt, 1H, *J* 10.42 and 8.43); 4.09 (dd, 2H, 10.45 and 7.00, *E*-H-3,5); 4.32 (dd, 2H, *J* 8.43 and 6.99, *Z*-H-3,5).

Allylperoxytricyclohexenyltin (28). δ(H) 4.50 (d, 2H, *J* 6.26); 5.33 (dm, 1H, *J* 10.80 and 2.51, *E*-H-3); 5.38 (dm, 1H, *J* 17.13 and 1.38, *Z*-H-3); 5.98 (ddt, 1H, *J* 17.15, 10.82 and 6.25, H-2).

3-(Tricyclohexylstannyl)allyl hydroperoxide (29). δ(H) 4.45 (d, 2H, *J* 6.83,

CH_2O); 6.21 (d, 1H, *J* 12.97, *J*(Sn) 63.03, H-1); 6.75 (dt, 1H, *J* 12.95 and 6.80, *J*(Sn) 139.4, H-2).

4-Tricyclohexylstannyl-1,2-dioxolane (30). δ(H) 2.30 (tt, 1H, *J* 11.61 and 8.09, H-4); 3.93 (dd, 2H, *J* 11.60 and 6.44, *E*-H-3,5); 4.36 (dd, 2H, *J* 8.05 and 6.45, *Z*-H-3,5).

Acetoxy(allylperoxy)dibutyltin (31). δ(H) 0.88 (t, 6H, *J* 7.24, CH_3); 1.33 (m, 4H, CH_2); 1.62 (m, 8H, CH_2CH_2); 2.04 (s, 3H, MeC=O); 4.47 (dt, 2H, *J* 6.10 and 1.22, CH_2O); 5.29 (dm, 1H, *J* 10.34 and 0.90, *E*-H-3); 5.35 (dm, 1H, *J* 17.26 and 1.40, *Z*-H-3); 5.94 (ddt, 1H, *J* 17.20, 10.55 and 6.15, H-2).

Allylperoxytriallyltin

The reaction of tetraallyltin with $^1O_2$ was carried out in an NMR tube, and monitored spectroscopically. The reaction of one molar equivalent of oxygen gave the allylperoxytin compound as the only significant product: δ(H) 4.46 (d, *J* 6.03, CH_2O); 5.28 (dm, *J* 16.65, 10.15 and 6.05).

Di(allylperoxy)mercury

Diallylmercury in $CDCl_3$ containing TPP was irradiated in an NMR tube with sodium light for 30 min while a stream of oxygen was passed through the solution. A grey deposit separated, which was presumably at least partially mercury. The NMR spectrum showed the solution to contain acrolein (77%) and di(allylperoxy)mercury, δ(H) 4.45 (d, 2H, *J* 6.24, CH_2O); 5.22 (d, 1H, *J* 10.35 and 0.95, *E*-H-3); 5.38 (dm, 1H, *J* 16.85 and 1.94, *Z*-H-3); 5.95 (ddt, 1H, *J* 16.85, 10.35 and 6.24, H-2).

1-Allyl-2-chloromercury-4-phenyl-1,2-dihydrotriazoline-3,5-dione

Allylmercury chloride in $CDCl_3$ was treated with PTAD to give the M-ene product, δ(H) 4.18 (d, 2H, *J* 6.58, CH_2N); 5.27 (dm, 1H, *J* 10.05 and 0.95, *E*-H-3); 5.35 (dm, 1H, *J* 16.50 and 1.27, *Z*-H-3); 5.80 (ddt, 1H, *J* 16.50, 10.05 and 6.58, H-2).

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