Ene Reactions of Allylic Tin Compounds with Singlet Oxygen and with 4-Phenyl-1,2,4-triazoline-3,5-dione

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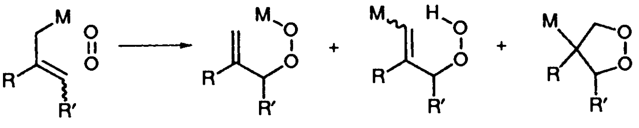
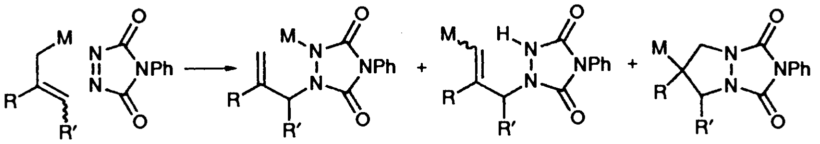
Allylic tin compounds (**I**) react with singlet oxygen to give allylperoxystannyl compounds (**II**) by stannylallylation, stannylallyl hydroperoxides (**III**) by hydroallylation, and 4-stannyl-1,2-dioxolanes (**IV**) by rearrangement and cycloaddition. For example, 3-trimethylstannylprop-1-ene (**I**; R = R′ = H; M = Me_3Sn) in CH_2Cl_2 at room temperature gives 25% **II**, 25% **III** and 50% **IV**; 1-tributylstannylcyclohex-2-ene (**I**; R–R′ = $-CH_2CH_2CH_2-$; M = Bu_3Sn) in CH_2Cl_2 gives 66% **II** and 33% **IV**, but in MeOH–benzene, the yield of **II** is >95%. The dioxolane **IV** appears to be a primary product of the reaction, and does not result from ring-closure of **II**. Under similar conditions, triethylsilylcyclohex-2-ene (**I**; R–R′ = $-CH_2CH_2CH_2-$; M = Et_3Si) in CH_2Cl_2 shows only the hydroallylation reaction to give **II**.



I **II** **III** **IV**

Similar reactions occur with 4-phenyl-1,3,4-triazoline-2,5-dione. For example, 3-trimethylstannylprop-1-ene in CH_2Cl_2 gives 85% **V** and 15% **VII**, but in MeOH–benzene, the yield of **V** is 95%. Under the same conditions, triethylsilylcyclohex-2-ene gives 5% **V**, 70% **VI**, and 25% of the cycloadduct **VII**.



I **V** **VI** **VII**

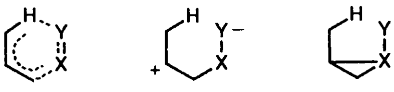
These reactions are discussed in terms of the usual mechanistic models for the ene reactions, and for the β-effect of organometallic groups.

The ene reaction involves hydroallylation of an enophile (X = Y) as shown in eqn. (1).[1,2] This process has found rather limited use in synthesis when the enophile is an alkene because of the rather low reactivity of most alkenes,[3] even when a Lewis acid is used as a catalyst.[4]

When the enophile is singlet oxygen, the reaction has been used widely as a route to allylic hydroperoxides because the reactivity and regio- and stereo-selectivity is often higher than that in the radical chain reaction of triplet oxygen.[5–9] Other enophiles which have been used include azo compounds such as azodicarboxylate esters[3] or triazolinediones, nitroso compounds, aldehydes, diethyl oxomalonate and sulphur dioxide.

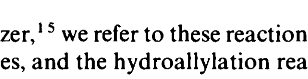
(1)

A great deal of attention has been paid to the mechanisms of these reactions, particularly when the enophile is singlet oxygen.[5–9] A one-step pericyclic process involving the transition state **1** is ruled out by the inter- and intra-molecular deuterium isotope effects which are observed with regiospecifically labelled alkenes,[8,10] and by the lack of stereoselectivity which is observed with certain enes.[11,12] An initial ene–enophile complex appears to be required, with a structure lying somewhere between the extreme forms **2** and **3**. A charge-transfer complex might also be acceptable.[13] Structure **3** is referred to as a perepoxide when X–Y = O–O, or as an aziridinium imide when X–Y = RN–NR.



1 **2** **3**

In organic reactions, organometallic substituents often simulate the behaviour of hydrogen, and in designing new organic reactions it is sometimes informative to consider hydrogen as a pseudometal.[14] In accord with this principle, we have looked for reactions involving metalloallylation of an enophile by eqn. (2).



(2)

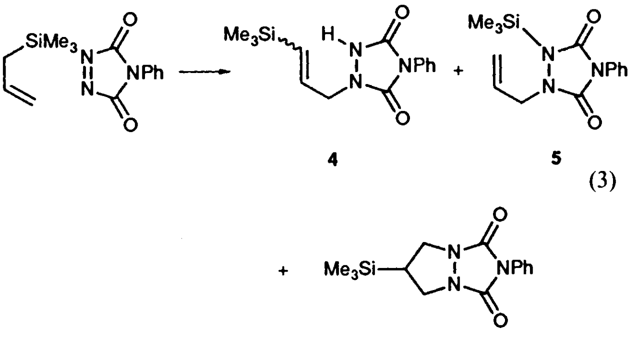
Following Oppolzer,[15] we refer to these reactions as metalloene, or M-ene processes, and the hydroallylation reactions as H-ene processes. With an almost unlimited range of metals and ligands it might be possible to enhance the reactivity and stereoselectivity so that the reactions might be more useful in synthesis. Further, we hoped that these reactions might provide some evidence for the mechanisms of ene reactions in general.

The stoichiometric M-ene reaction of allyl-lithium, -magnesium, and -zinc compounds with alkenes has been known since 1970,[16] and its intramolecular variant is proving to be useful in organic synthesis.[15] A modification in which the allylmetallic compound is generated *in situ* with a catalytic amount of a nickel(0), palladium(0) or platinum(0) compound holds out further promise.[15]

The metalloallylation of aldehydes[17] with allyl-magnesium, -boron,[18,19] -tin,[20,21] -germanium, and -silicon[22] reagents is a well-established synthetic procedure; the mechanisms are usually discussed in terms of the transition state **1**.

It seemed likely that with suitably ligated metals, metalloallylation of singlet oxygen or azo compounds should occur, but little work appears to have been reported in this field.[23] A number of studies have been made of the reaction of singlet oxygen with allylsilanes[24–29] and allylgermanes,[24,25,29] but these have all shown migration of hydrogen geminal to the metal, rather than of the organometallic group itself. Schenck treated triphenyl(3-methylbut-2-enyl)tin with singlet oxygen, but similarly reported only H-ene products.[30] We have not been able to locate any examples in the literature of an M-ene reaction involving singlet oxygen.

Similarly a number of studies have been reported of the reaction of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) with allylsilanes[24,27,28,31–33] and allylgermanes,[24–34] but again these reactions show hydroallylation. The single example of metalloallylation of an azo compound which we have been able to find[33] is the reaction of allyltrimethylsilane with PTAD which shows products resulting from hydroallylation (**4**), metalloallylation (**5**), and cycloaddition with a shift of the metal (**6**), in ratios which depend on the temperature and the nature of the solvent.



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We report here a study of the reactions of singlet oxygen and of PTAD with 3-trimethylstannylprop-1-ene (**7**), 4-triphenylstannylbut-2-ene (**8**), cyclohexene (**9**), 1-triethylsilylcyclohex-2-ene (**10**), 1-trimethylstannylcyclohex-2-ene (**11**), 1-tributylstannylcyclohex-2-ene (**12**) and 1-triphenylstannylcyclohex-2-ene (**13**).

7

8

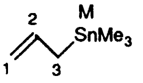
Results and Discussion

Preparation and Conformations of Metallocyclohexenes (**10**–**13**).—Homolytic addition of trimethyltin hydride or of triphenyltin hydride to cyclohexa-1,3-diene has been reported to give **11**[35] and **13**[36] as a mixture with the alternative 1,2-adducts, but the products were not separated. A general route to the trialkylstannylcyclohexenes involves the reaction of trialkylstannyl-lithium or -sodium with 1-halogenocyclohex-2-enes which are obtained by reduction of cyclohexenones followed by halogenation.[37–40]

Table 1 ^{119}Sn, ^{29}Si and ^{13}C NMR spectra of allylmetallic compounds[a]

	7	10	11	12	13
δ(Si or Sn)	−4.6	6.48	−3.0	−21.6	−130.7
δ(C-1)	109.40	25.14	26.42	26.01	28.89
($J_{^{117}Sn}$)	(49.1)		(336.2)	(283.1)	(270.2)
($J_{^{119}Sn}$)			(351.6)	(297.5)	(387.0)
δ(C-2)	137.60	128.45	130.87	131.57	129.80
(J_{Sn})	(47.2)		(47.5)	(38.0)	(44.5)
δ(C-3)	18.05	125.00	121.80	121.45	124.25
($J_{^{117}Sn}$)	(283.1)		(49.5)	(43.5)	(53.5)
($J_{^{119}Sn}$)	(296.2)				
δ(C-4)		24.00	24.96	25.00	24.86
(J_{Sn})			(14.7)	(13.4)	(16.2)
δ(C-5)		23.00	22.80	23.24	23.05
(J_{Sn})			(21.2)	(20.0)	(26.0)
δ(C-6)		23.04	26.39	26.80	26.68
(J_{Sn})			(16.9)	(16.2)	(19.1)
δ(C-α)	−10.35	2.42	−10.50	8.98	139.00
($J_{^{117}Sn}$)	(314.2)		(293.0)	(286.4)	(439.0)
($J_{^{119}Sn}$)	(328.3)		(306.5)	(299.3)	(460.0)
δ(C-β)		7.61		29.23	132.27
(J_{Sn})				(20.1)	(33.1)
δ(C-γ)				27.50	128.45
(J_{Sn})				(52.3)	(46.6)
δ(C-δ)				13.72	128.82
(J_{Sn})				(<5)	(11.3)

[a] The molecules are labelled as illustrated:



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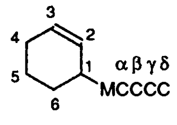
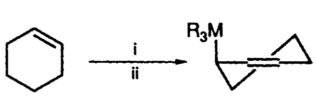


10–13

We have found that the organometallic group can be introduced by metallation of cyclohexene with Schlosser's base [BuLi/Bu^{t}OK/*N,N,N',N'*-tetramethylethylenediamine (TMEDA)],[41,43] followed by treatment with the appropriate organometallic halides, when compounds **10**–**13** were obtained in 80–95% yield [eqn. (4)].



(4)

9

10 $R_3M = Et_3Si$
11 $R_3M = Me_3Sn$
12 $R_3M = Bu_3Sn$
13 $R_3M = Ph_3Sn$

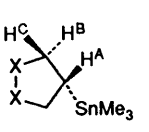
Reagents: (*i*) BuLi/Bu^{t}OK/TMEDA; (*ii*) R_3MX

Kitching *et al.*[40] showed by NMR spectroscopy that, in solution, **13** has a quasi-axial Ph_3Sn group, although, in the crystal, this group is quasi-equatorial. We have carried out a detailed ^{119}Sn, ^{29}Si and ^{13}C NMR study of the metalloallyl compounds **7** and **10**–**13** in solution, and the results are shown in Table 1.

Table 2 ^{1}H NMR spectra of cyclic adducts[a]

		H^A		H^B		H^C		H^D	
Compd.[a]	X=X	δ	J_{AB}	δ	J	δ	J	δ	J_{BC}
16	O_2	2.30 (tt)	11.30	3.75 (dd)	7.71 (AC)	4.30 (dd)	6.96 (BC)		
19	O_2	2.59 (ddd)	9.60	4.51 (dd)	10.40 (AC)	3.11 (dd)	7.36 (AD)	4.82 (dq)	8.50
22	PTAD	1.91 (tt)	12.63	3.41 (dd)	7.51 (AC)	4.19 (dd)	11.48 (BC)		
25	PTAD	2.68 (ddd)	7.68	4.39 (dd)	13.20 (AC)	3.78 (dd)	6.80 (AD)	4.81 (dq)	11.29
33	O_2	2.15 (m)		4.64 (t)	4.89				
35	PTAD	1.65 (m)		4.63 (t)	4.43				
39	O_2	2.14 (m)		4.63 (t)	4.83				
41	O_2	2.89 (m)		4.93 (t)	4.77				
43	PTAD	1.62 (m)		4.50 (t)	4.50				
45	PTAD	2.38 (m)		4.93 (t)	4.42				

[a] The molecules are labelled as illustrated:



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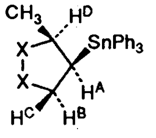

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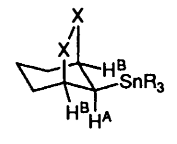
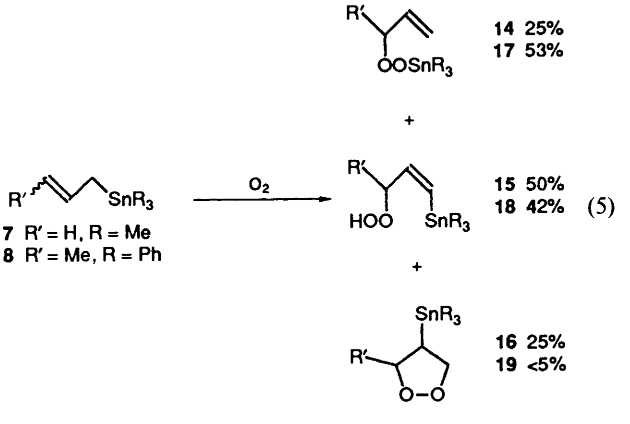


33, 35, 39, 41, 43, 45

The data for **13** and the ^{13}C chemical shifts for **11**, agree with those in the literature,[38,40] which indicate that the stannyl groups prefer a quasi-axial orientation. Similarly the values for ^3J(Sn–C5) (20.0 Hz) and of J(H1–H2) (4.85 Hz) for **12**, which were determined by spin decoupling, show that this compound has the same conformation as **11** and **13**. It has been reported that the Ph_3Sn group in 3-triphenylstannylprop-1-ene is oriented nearly orthogonally to the plane of the allyl system,[39] and in all these allyltin compounds the conformation in solution appears to be dominated by the stabilisation which results from maximising the σ_{C-Sn}–π hyperconjugation.

Unfortunately it is still difficult to deduce the conformation of **10** from the NMR data, but comparison with the ^{13}C NMR spectrum of trimethylsilylcyclohex-2-ene[38] suggests that **10** similarly prefers a quasi-axial orientation of the R_3Si group.

Reactions with Singlet Oxygen and with 4-*Phenyl*-1,2,4-*triazoline*-3,5-*dione*.—The allylic tin compounds **7**[44] and **8**[45] (Z:E = 1:1) reacted with $^1O_2$ [tetraphenylporphine (TPP), −20 °C] and with PTAD in CH_2Cl_2 to give the products shown in eqns. (5) and (6).



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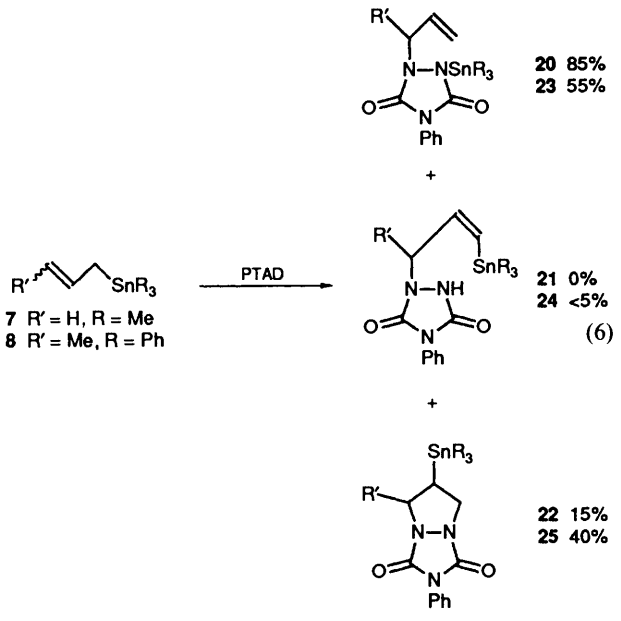


(6)

The products **14** and **17** from metalloallylation of oxygen were hydrolysed to the hydroperoxides during chromatography on silica gel, and were identified as the corresponding alcohols after reduction. Similarly the PTAD adducts **20** and **23** gave the corresponding protic products on separation. The dioxolane **16** could not be isolated because it decomposed on silica gel (see below), but the corresponding dihydropyrazines **22** and **25** were stable and were isolated and identified.

Taking **22** as an example, the ^{1}H NMR spectrum (Table 2) shows three sets of peaks for the ring protons in a ratio of 2:2:1 [Fig. 1(*c*)]. The high-field signal (1 H) was reduced to a triplet with J = 12.6 or 7.5 Hz when either of the other two signals (2 H) were irradiated, showing that this proton couples with two pairs of protons, in *trans* and *cis* positions, respectively. The ^{13}C NMR spectrum (Table 3) shows the presence of only one type of carbonyl group, confirming the symmetry of the structure. The presence of the trimethylstannyl group was confirmed by the observation of $^{117/119}$Sn satellites in the ^{1}H NMR spectrum, and of a ^{119}Sn signal at δ = 0.88.

The dioxolane **16** was then identified by comparison of the ^{1}H NMR spectrum with that of **22** (Table 2) which shows similar coupling constants and spin-decoupling behaviour. The analysis of the spectra of both **22** and **16** were confirmed by spin simulation.

Partial ^{1}H NMR spectra of **15** (isolated from silica gel) and **22** are shown in Fig. 1. The preferred *cis* configurations of **15** and **18**

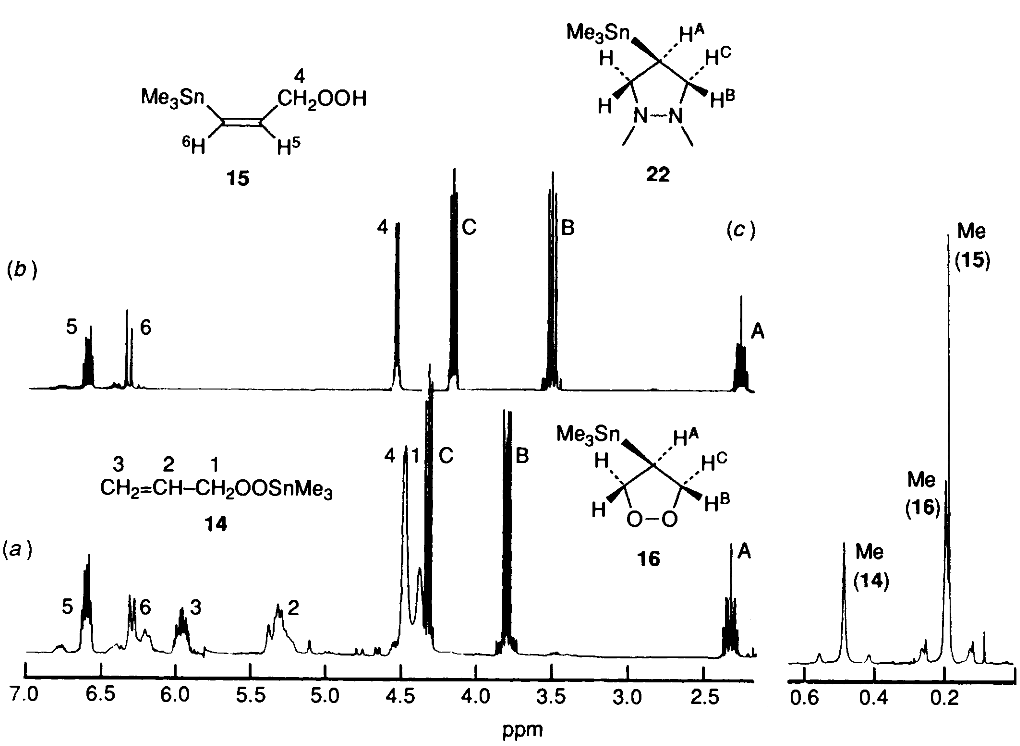


Fig. 1 ^1H NMR spectra: (*a*) products of the reaction of allyltrimethylstannane (**7**) with $^1O_2$ in CH_2Cl_2; (*b*) partial spectrum of the hydroperoxide **15**; (*c*) partial spectrum of the dihydropyrazole **22**. The numbering of the hydrogen atoms and of the corresponding peaks in the spectra are arbitrary.

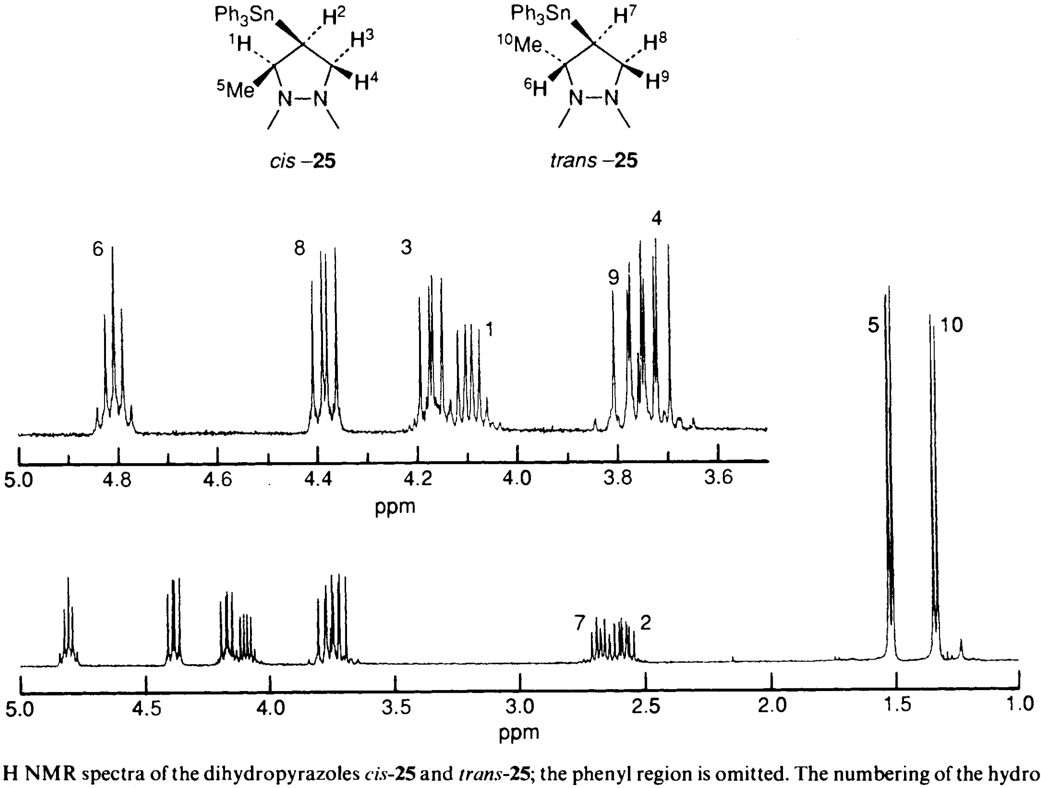


Fig. 2 Partial ^1H NMR spectra of the dihydropyrazoles *cis*-**25** and *trans*-**25**; the phenyl region is omitted. The numbering of the hydrogen atoms and of the corresponding peaks in the spectra are arbitrary.

were determined from values of *J*(Sn–H) and the coupling constants of the vinylic protons (see the Experimental section); for **18** the ratio of *cis*:*trans* isomers is 10:1. A partial ^1H NMR spectrum of **25**, which was isolated chromatographically is shown in Fig. 2. The structure was determined by spin-decoupling and spin-simulation: two isomers are present, in the ratio of 2:1, in which the Me and Ph_3Sn groups are mutually *trans* or *cis*, respectively.

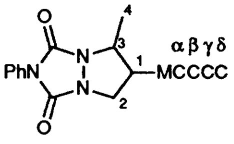
In order to investigate further the effect of the conformation of the ene and of the nature of the organometallic group, the reactions of **9** and of the organometallic cyclohexenes **10**, **11**, **12** and **13**, were studied.

Cyclohexene (**9**) reacted with $^1O_2$ (TPP, CH_2Cl_2) at room temperature to give 3-hydroperoxycyclohexene **26** in 30% yield after 8 h, and with PTAD (1 equiv., CH_2Cl_2) to give the triazolidine **27** in quantitative yield [eqn. (7)].[46]

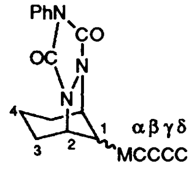
Table 3 ^{119}Sn, ^{29}Si and ^{13}C NMR spectra for dihydropyrazines[a]

	22	*cis*-**25**	*trans*-**25**	**30**	**35**	**43**	**45**
δ(Si or Sn)	0.88	−117.15	−120.37	2.70	−14.41	−32.05	−127.25
δ(C-1)	25.48	35.77	34.82	38.94	39.17	38.69	41.07
$(J_{^{117}\mathrm{Sn}})$	(264.4)	(330.74)	(345.0)		(300.0)	(236.7)	(344.4)
$(J_{^{119}\mathrm{Sn}})$	(280.9)				(314.1)	(247.4)	(361.0)
δ(C-2)	50.60	48.49	48.50	60.45	61.81	61.84	61.13
δ(C-3)		58.92	57.85	27.54	28.85	29.05	29.29
δ(C-4)		19.21	21.17	18.46	18.68	18.70	18.47
δ(C-α)	−10.90	135.07	135.97	4.28	−8.84	9.94	136.58
$(J_{^{117}\mathrm{Sn}})$	(330.0)				(334.0)	(321.5)	(507.1)
$(J_{^{119}\mathrm{Sn}})$	(344.5)				(349.6)	(336.5)	(530.7)
δ(C-β)		137.00	136.88	7.55		29.03	136.91
(J_{Sn})						(8.7)	(36.8)
δ(C-γ)		129.19	129.15			27.25	129.14
(J_{Sn})						(62.3)	(51.6)
δ(C-δ)		129.91	129.78			13.40	129.68
(J_{Sn})							(10.2)
δ(C-*i*)	131.81	131.79	131.81	131.98	131.92	131.90	131.82
δ(C-*o*)	129.03	129.00	129.09	129.04	129.10	129.00	129.10
δ(C-*m*)	125.33	125.43	125.48	125.38	125.51	125.35	125.48
δ(C-*p*)	127.95	127.90	128.04	127.93	128.06	127.85	128.09
δ(C=O)	155.40	152.52 152.83	154.38 154.80	155.99	156.63	156.31	156.19

[a] For the purpose of this table, the molecules are labelled as illustrated:



cis – /*trans* – **25**



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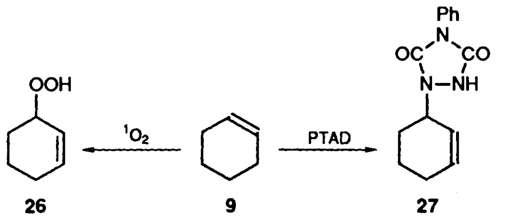

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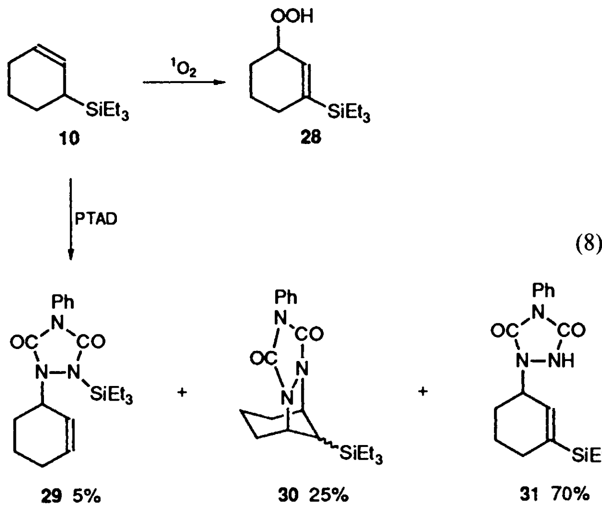

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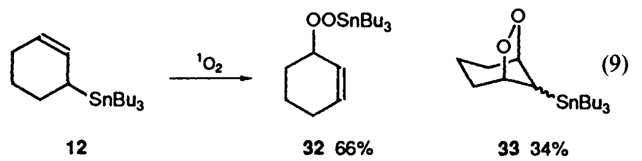
Under the same conditions, **10** reacted with $^1O_2$ by hydro-allylation to give only the hydroperoxide **28** in 65% yield after 5 h and with PTAD (in 3 min) to give the three products **29**–**31** as shown in eqn. (**8**).

Under the same conditions, the tributyltin compound **12** reacted rapidly (1.5 h) with $^1O_2$ to give the peroxide **32** and the dioxolane **33** [eqn. (9)], and with PTAD it reacted immediately on mixing to give the stannyltriazolidine **34** and the cycloadduct **35** [eqn. 10)]; in neither case was there any evidence of a hydro-allylation component in the reactions.

These results show that both the reactivity and the nature of the products vary greatly as M in eqn. (2) is changed from H to R_3Si, and R_3Sn.

The products **32** and **34** of stannylallylation were hydrolysed to the corresponding protic compounds **26** and **27** during chromatography on silica gel. The PTAD adduct **35** could be isolated, but the endoperoxide **33** decomposed to cyclohex-2-enone **37**. It has been reported that 6,7-dioxabicyclo[3.2.1]-heptane has a half-life of 2.7 h, and rearranges on silica gel to give 3-hydroxycyclopentanone [eqn. (11)].[47]

When the products of eqn. (9) were monitored by ^1H NMR spectroscopy the intensity of the triplet at $\delta = 4.64$ for the endoperoxide **33** decreased, and a new set of peaks at $\delta = 4.12$ appeared; there was no change in the intensity of the signals relating to the stannyl peroxide **32**. The chemical shift of the new peaks is close to that of the 3-H proton ($\delta = 4.10$) for 3-



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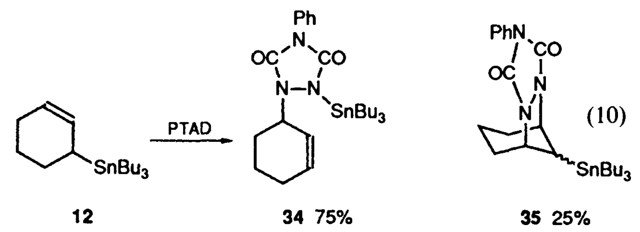

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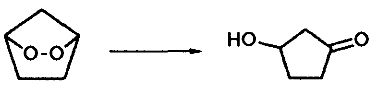

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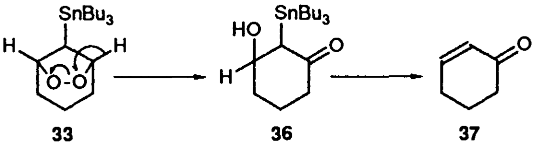
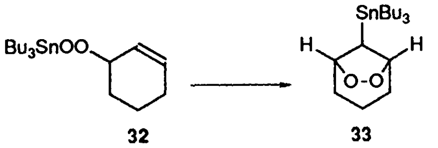


(12)

hydroxycyclohexanone.[48] This suggests that, on silica gel, the endoperoxide **33** decomposes to the stannyl hydroxy ketone **36**, followed by elimination of tributyltin hydroxide to give the cyclohexenone **37**.

The formation of **33** might be envisaged to occur by either homolytic or heterolytic intramolecular addition of **32** [eqn. (13)]. A homolytic process has already been discounted for the allylic isomerisation of an allylic hydroperoxide,[49–50] but allyl hydroperoxides do undergo ring closure in the presence of mercury(II) salts to give 4-mercurio-1,2-dioxolanes [eqn. (14)].[51–55]



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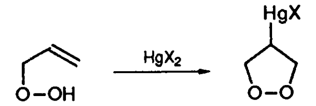
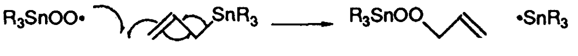


(14)

The hydroperoxide **26** was therefore treated with tributyltin methoxide to give **32**, which was then allowed to stand under the conditions of the ene reaction, and monitored by NMR spectroscopy; no such ring closure was observed.

It was also feasible that the peroxytin compounds could be formed by a radical chain process involving either singlet or triplet oxygen [eqns. (15) and (16)].

$$R_3Sn^{\bullet} + O_2 \longrightarrow R_3SnOO^{\bullet} \qquad (15)$$



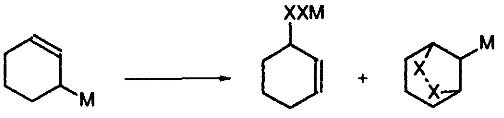
(16)

Less plausible homolytic routes to the *endo*-peroxide **33** can also be envisaged. However, 2,6-di-*tert*-butyl-4-methylphenol had no effect on the rate or the products of the reaction of **12** with $^1O_2$, and an attempt to establish a chain reaction with $^3O_2$ showed a negligible amount of reaction (< 5% after 8 h).

In order to obtain further evidence for the reaction mechanism, the effect of temperature and of solvent on the reaction of **12** with $^1O_2$ and PTAD was studied. The results are shown in Table 4.

A decrease in temperature gave a decrease in the proportion of the M-ene products **32** and **34**, and an increase in the yield of the cyclic adducts **33** and **35**. In a more polar solvent (methanol–benzene), there was a remarkable change in the product composition; the methanol was not involved in the reaction, but the M-ene products **32** and **34** were formed in near-quantitative yield.

The effect of the ligands on the tin on the reaction of the stannylcyclohexenes **11–13** with O_2 and with PTAD at −20 °C [eqn. (17)] are shown in Table 5.



(17)

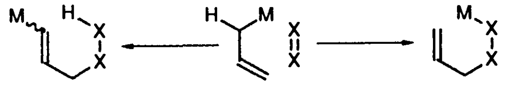
11–13 X=X = O=O **32,38,40** **33,39,41**
X=X = PTAD **34,42,44** **35,43,45**

None of the reactions gave any evidence of the hydroallylation process. The ligands on the tin had a substantial effect on the yields of products, and as the organotin group was changed from Me_3Sn, through Bu_3Sn, to Ph_3Sn, the proportion of the M-ene products decreased, and that of the cyclic adducts increased.

Discussion

The principal observations which have come out of this work are as follows.

(1) Allyltin compounds will react with $^1O_2$ and PTAD by both M-ene and H-ene chemistry and in a polar solvent (MeOH–benzene) the M-ene path is followed almost exclusively.



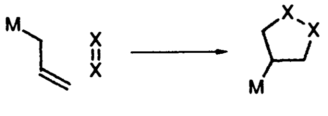
(18)

(2) Allylsilicon compounds show similar M-ene and H-ene reactions with PTAD, but we have not yet observed an M-ene reaction with singlet oxygen.

(3) When both M-ene and H-ene reactions occur, they involve only one allylic system, *i.e.* only hydrogen which is geminal to the metal is transferred.

(4) When both M-ene and H-ene reactions occur, they are faster than is the H-ene reaction in the absence of the metal substituent.

(5) Allyltin compounds can react with $^1O_2$ and PTAD by cycloaddition across the allylic system, accompanied by 1,2-rearrangement of the metal.



(19)

(6) Allylsilicon compounds show a similar rearrangement–cycloaddition reaction with PTAD, but we have not yet observed this reaction with $^1O_2$.

We chose to discuss these reactions in terms of the perepoxide

Table 4 The effects of temperature and solvent on the yields of **32**–**35** in the reaction of **12** with $^1O_2$ and PTAD

T/°C	Solvent	Yield (%)			
		32[a]	**33**[a]	**34**[b]	**35**[b]
25	CH_2Cl_2	80	20	75	25
25	MeOH–C_6H_6	95	<5	95	5
−20	CH_2Cl_2	76	24	65	35
−40	CH_2Cl_2	68	32	—	—

[a] X=X = $^1O_2$. [b] X=X = PTAD.

Table 5 Products of the reaction of the stannylcyclohexenes **11**–**13** with $^1O_2$ and PTAD in CH_2Cl_2 at −20 °C

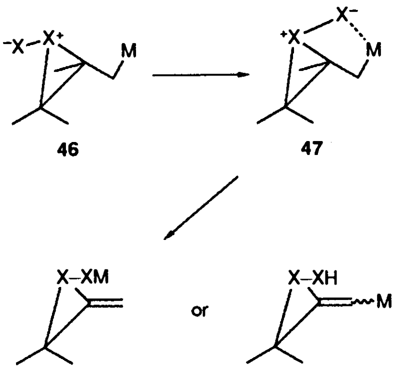
Compound	R_3M	X=X	Product (% Yield)	
11	Me_3Sn	$^1O_2$	**38** (85)	**39** (15)
12	Bu_3Sn	$^1O_2$	**32** (76)	**33** (24)
13	Ph_3Sn	$^1O_2$	**40** (64)	**41** (36)
11	Me_3Sn	PTAD	**42** (80)	**43** (20)
12	Bu_3Sn	PTAD	**34** (75)	**35** (25)
13	Ph_3Sn	PTAD	**44** (63)	**45** (37)

and aziridinium imide intermediates **3** which are currently favoured for the ene reactions of hydrocarbons, but with only slight modifications the same arguments could equally well be expressed in terms of a one-step pericyclic mechanism. We note that some caution must be exercised in discussing the structures of allylperoxy compounds because they are potentially capable of undergoing allylic rearrangements by a radical chain mechanism [eqn. (20), M = H or metal].[49,56–58]

(20)

However, these reactions do not appear to be important under our reaction conditions. The products of H-ene reactions of PTAD do not show such rearrangements.[12]

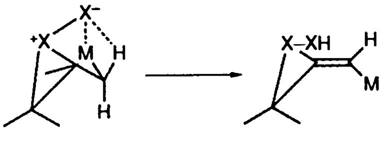
It appears that of the two isomeric intermediates **46** and **47**, which can be envisaged, the products, whether H-ene or M-ene, are formed only through **47**; (we note, however, that there are examples in the literature of allylsilanes and allylgermanes which show shift of non-geminal hydrogen).[59]



(21)

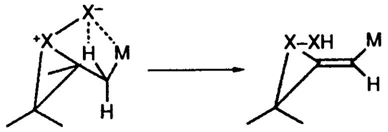
We postulate that this results from stabilization of **47** by coordination of the terminal X to the metal. Some form of attractive interaction is often assumed between X and H in these intermediates, but the interaction with a metal would be expected to be much stronger.

The H-ene reaction would involve the rotamer **48** which would give a Z-alkene product, or **49** which would give an E-alkene product.



48

(22)



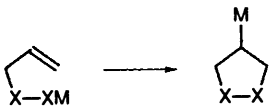
49

(23)

We have observed only the former of these two stereoselectivities, but there are examples in the literature of the H-ene reactions of allylsilanes and allylgermanes which give preferentially the E-product;[59] with bulky substituents on the ene and on the metal, the conformer **48** may be the less sterically hindered.

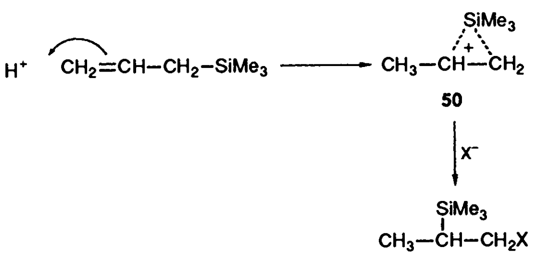
The reactions which formally involve shift of the metallic group and an addition of X=X across the ends of the three-carbon system came as a surprise, and the only precedent which we have been able to find is the reaction involving an allylsilane and PTAD [eqn. (3)];[33] we can find no examples in the literature of the equivalent shift of hydrogen accompanying the ene reactions of singlet oxygen, PTAD, or any other enophile.

One obvious possibility was that these products might arise by ring-closure of the products of the M-ene reaction [eqn. (24)], but we could not observe such ring closures with our allylperoxy-silicon or -tin compounds under either homolytic or heterolytic conditions. Similarly we could find no evidence for the formation of 1,2-dioxetanes or diazetidines, and it seems unlikely that these compounds are involved in the formation of the five-membered ring: the dioxolanes or dihydropyrazoles appear to be primary products of the reaction.



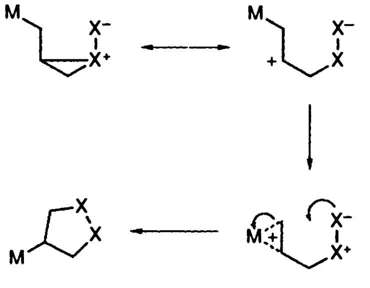
(24)

We believe that this ring-closure reaction may be another manifestation of the familiar β-effect in which an organometallic group anchimerically assists the formation of a carbenium ion by forming a bridged intermediate.[60,61] For example, allylsilanes undergo very rapid protonation to form the intermediate **50**.[62,63] Although we can find no example in the literature, such a reaction is potentially capable of giving a product in which the metal has migrated to the central carbon atom [eqn. (25)].



(25)

Singlet oxygen and PTAD similarly act as electrophiles towards the ene, and their attack can be envisaged to be accompanied and accelerated by the formation of the bridged carbenium ions **51**. Nucleophilic attack by X on the terminal carbon would then generate the five-membered ring with displacement of the metal onto C-2 [eqn. (26)].



(26)

51

Conclusion

This work has yielded the first M-ene reactions of $^1O_2$, a new route to alkylperoxy silicon and tin compounds, and a route to the new 3-silyl- and 3-stannyl-1,2-dioxolanes, and 3-stannylallyl hydroperoxides. Allylmetallic compounds are gaining increasing importance in organic synthesis. With the almost unlimited variety of combinations of metals and ligands which are available, we hope that it will be possible to direct these reactions so that they can be made to be selective for each of the three types of product, and can be developed into useful synthetic procedures. We also hope that these studies will throw some light on the vexed question of the ene reaction, and by an appropriate choice of metal and ligands, it may be possible to detect directly the postulated perepoxide and aziridinium imide intermediates. These problems are being investigated.

Experimental

^{1}H, ^{13}C, ^{29}Si and ^{119}Sn NMR spectra were recorded for solutions in $CDCl_3$ on a Varian VXR-400 spectrometer. ^{1}H and ^{13}C chemical shifts were measured relative to the solvent using δ_H = 7.24 and δ_C = 77.00; ^{29}Si spectra were referenced to tetramethylsilane (0.00 ppm) and ^{119}Sn spectra to tetramethylstannane (0.00 ppm). Coupling constants are in Hz. Mass spectra were recorded on a VG 7070H spectrometer, and IR spectra on a Perkin-Elmer PE983 instrument. Column chromatography was carried out on Merck silica gel 60 (70–230 mesh).

3-*Trimethylstannylprop*-1-*ene* (**7**).—This was prepared by the reaction of allylmagnesium bromide with trimethyltin chloride.[44] δ_H 0.08 (9 H, s, $J_{^{119}Sn}$ 53.5, $J_{^{117}Sn}$ 51.2), 1.75 (2 H, ddd, *J* 8.60, 1.05, and 0.50, $J_{^{119}Sn}$ 57.5, $J_{^{117}Sn}$ 54.7), 4.65 (1 H, ddt, *J* 10.00, 2.15, 0.50), 4.77 (1 H, ddt, *J* 16.85, 2.15, 1.05) and 5.90 (1 H, ddt, *J* 16.85, 10.00, 8.60); for δ_C, see Table 1.

1-*Triphenylstannylbut*-2-*ene* (**8**).—Octa-2,6-diene was a major product when the Grignard reagent was prepared from crotyl bromide in the usual way, whilst hexaphenylditin was produced in large amounts if triphenyltin chloride in ether was added to magnesium before the crotyl bromide. The best way to prepare this compound was to add dropwise a solution of crotyl bromide (5 g, 37 mmol; a fivefold excess) and triphenyltin chloride (3 g, 7.8 mmol) to magnesium (1 g, 41 mmol) in tetrahydrofuran (THF) (10 cm^3) at a rate sufficient to maintain gentle refluxing under argon. After work-up, the crude product was chromatographed on silica gel using pentane as the eluent, to give **8** in 85% yield, m.p. 50 °C (lit.,[45] 51–52 °C). This consisted of a 1:1 mixture of *E*- and *Z*-isomers. δ_H 1.47 (dm, *J* 6.77, 0.84), and 1.59 (dm, *J* 6.39, 1.55, CH_3), 2.37 (dm, *J* 8.23, 1.31), 2.40 (dm, *J* 8.95, 1.44, CH_2), 5.26 and 5.70 (both m, =CH in one isomer), 5.38 and 5.70 (=CH in the other isomer), 7.35 (9 H, m) and 7.52 (6 H, m); δ_C 11.95 and 12.61 (CH_3), 16.00 and 17.81 (CH_2), 121.01 and 127.75 (=C in one isomer), 123.14 and 126.85 (=C in the other isomer), 128.44, 128.89, 128.93, 137.02, 137.10 and 138.75; δ_{Sn} −121.62 and −121.45.

Synthesis of Cyclohexenylmetallic Compounds **10**, **11**, **12** and **13**.—The general procedure was as follows. Butyllithium (10 mmol) in hexane was syringed into a mixture of Bu^{t}OK (12 mmol) and cyclohexene (20 cm^3) at −75 °C under argon. Tetramethylethylenediamine (12 mmol) was then added, and the mixture was allowed to warm to room temperature and stirred for 5–8 h.

The appropriate trialkyl-silicon or -tin chloride [the solid Ph_3SnCl in THF (10 cm^3)] was then added dropwise at −30 °C. The mixture was stirred at room temperature for 2 h, then hydrolysed with 5% aqueous ammonium chloride. The product was extracted into ether, and washed with water. The solvent was removed and the products were separated in 80–95% yield by chromatography on silica gel, and distilled or recrystallised from ethanol or methanol. Values for δ_C, $\delta_{^{29}Si}$ and $\delta_{^{119}Sn}$ are given in Table 1; other characteristics were as follows.

3-*Triethylsilylcyclohexene* (**10**). B.p. 135 °C/18 mmHg; δ_H 0.55 (6 H, q, *J* 7.86), 0.94 (9 H, t, *J* 7.86), 1.48 (2 H, m), 1.65 (1 H, m), 1.74 (2 H, m), 1.96 (2 H, m), 5.58 (1 H, dm, *J* 10.10, 3.99) and 5.64 (1 H, dm, *J* 10.10, 1.80); ν_{max}(neat)/cm^{-1} 2944, 2929, 2864, 1456, 1239, 1015 and 892; *m*/*z* (70 eV) 196 (M$^{\cdot+}$, 8%), 167 (4), 115 (92) and 87 (100).

3-*Trimethylstannylcyclohexene* (**11**).[38] B.p. 75 °C/30 mmHg; δ_H 0.06 (9 H, s, $J_{^{119}Sn}$ 51.53, $J_{^{117}Sn}$ 49.26), 1.52 (1 H, m), 1.66 (1 H, m), 1.78 (1 H, m), 1.92–2.15 (4 H, complex), 5.43 (1 H, dm, *J* 9.89, 1.84) and 5.72 (1 H, dm, *J* 9.89, 2.08).

3-*Tributylstannylcyclohexene* (**12**). B.p. 198–200 °C/18 mmHg; δ_H 0.86 (6 H, t, *J* 7.35), 0.87 (9 H, t, *J* 7.30), 1.29 (6 H, m), 1.45 (8 H, m), 1.64 (1 H, m), 1.77 (1 H, m), 1.99 (2 H, m), 2.13 (1 H, m, J_{Sn} 80), 5.38 (1 H, dm, *J* 10.08 , 3.93) and 5.73 (1 H, dm, *J* 10.08, 2.18); ν_{max}/cm^{-1} 2951, 2915, 2843, 1456, 1373, 1069 and 874; *m*/*z* (70 eV) 315 (M$^{\cdot+}$ 57%) and 179 (100) (Found: C, 58.35; H, 9.8. $C_{18}H_{36}Sn$ requires C, 58.25; H, 9.77%).

3-*Triphenylstannylcyclohexene* (**13**). M.p. 81–82 °C (lit.,[38] 79–80.5 °C); δ 1.65 (2 H, m), 1.88–2.36 (4 H, complex), 2.89 (1 H, m, J_{Sn} 89), 5.57 (1 H, dm, *J* 9.90, 1.62), 5.98 (1 H, dm, *J* 9.90, 2.18), 7.35 (9 H, m) and 7.54 (6 H, m).

Photo-oxygenation.—General procedure. The photo-oxygenation was carried out in a temperature-controlled cell, using a 400 W sodium lamp, and TPP as the sensitizer in CH_2Cl_2, or Rose Bengal in methanol–benzene. The singlet oxygenation was also performed in $CDCl_3$ in an NMR tube to determine the reaction time and the product ratio. The progress of the reaction was followed by TLC. When the reaction was complete, any solid was filtered off and washed with solvent. The solvent was removed from the combined filtrates and the residue was chromatographed on silica gel, using a solvent mixture of pentane–CH_2Cl_2 (5:1 v:v), to give the following products.

Prop-2-enyl trimethylstannyl peroxide (**14**). δ_H 0.49 (9 H, s, J_{Sn} 56.7), 4.40 (2 H, m), 5.30 (2 H, m), 5.76 (1 H, m); $\delta_{^{119}Sn}$ 157.44. This compound is moisture-sensitive. It was reduced in the NMR tube with triphenylphosphine, then treated with a drop of trifluoroacetic acid. The spectrum was then consistent with that of allyl alcohol.

(Z)-3-*Trimethylstannylprop-2-enyl hydroperoxide* (**15**). Viscous oil. δ_H [see also Fig. 1(*a*)] 0.19 (9 H, s, $J_{^{119}Sn}$ 56.0, $J_{^{117}Sn}$ 53.5), 4.48 (2 H, dd, *J* 6.24, 0.91, J_{Sn} 15.0), 6.31 (1 H, dt, *J* 12.90, 0.91, $J_{^{119}Sn}$ 57.12, $J_{^{117}Sn}$ 54.66), 6.59 (1 H, dt, *J* 12.90, 6.24, $J_{^{119}Sn}$ 142.03, $J_{^{117}Sn}$ 135.67), 7.69 (1 H, s, OOH; $J_{^{119}Sn}$ 180.9, $J_{^{117}Sn}$ 173.0); δ_C −8.39 ($J_{^{119}Sn}$ 355.7, $J_{^{117}Sn}$ 339.7), 78.79 (J_{Sn} 43.9), 138.14 ($J_{^{119}Sn}$ 408.5, $J_{^{117}Sn}$ 389.6) and 141.25; $\delta_{^{119}Sn}$ −53.96; *m*/*z* (70 eV, FAB, *m*-nitrobenzyl alcohol) 392 (M$^+$ + 1). This compound was not stable and after several h at room temperature it deposited a tin compound.

4-*Trimethylstannyl*-1,2-*dioxolane* (**16**). $\delta_{^{119}\mathrm{Sn}}$ −4.25. The ^{1}H NMR spectra are given in Fig. 1 and Table 2. The compound decomposed on silica gel to give acrolein.

But-3-*en*-2-*yl triphenylstannyl peroxide* (**17**). On silica gel, this gave but-3-en-2-yl hydroperoxide. δ_H 1.79 (3 H, 2 d, *J* 7.49, 7.98), 4.59 (1 H, m), 5.17 (1 H, dd, *J* 10.35, 1.20), 5.20 (1 H, dd, *J* 17.20, 1.20), 5.82 (1 H, ddd, *J* 17.20, 10.20, 7.68) and 7.60 (1 H, br, OOH); δ_C 16.18, 85.35, 118.67 and 138.50. The hydroperoxide was then reduced with Ph_3P, and was found to be identical with but-3-en-2-ol, prepared by reduction of but-3-en-2-one.[64] δ_H 1.24 (3 H, two d, *J* 6.40, 6.39), 1.70 (1 H, br, OH), 4.28 (1 H, m), 5.03 (1 H, dm, *J* 10.47, 1.27), 5.18 (1 H, dm, *J* 17.16, 1.27) and 5.87 (1 H, ddd, *J* 17.15, 10.45, 6.40).

1-*Methyl*-3-*triphenylstannylprop*-2-*enyl hydroperoxide* (**18**). Although it was chromatographed three times, this compound was still contaminated with a small amount of the hydroperoxide from **17**. δ_H 1.13 (3 H, d, *J* 6.46), 4.41 (1 H, ddq, *J* 6.80, 1.12, 6.46), 6.48 (1 H, dd, *J* 12.76, 1.12, $J_{^{119}\mathrm{Sn}}$ 80.4, $J_{^{117}\mathrm{Sn}}$ 76.9), 6.70 (1 H, dd, *J* 12.76 and 6.80, $J_{^{119}\mathrm{Sn}}$ 168.5, $J_{^{117}\mathrm{Sn}}$ 161.1), 7.15 (1 H, br, OOH), 7.40 (9 H, m) and 7.60 (6 H, m); δ_C 18.56, 83.46, 128.65, 129.06, 129.95 and 136.87 (four aromatic carbons), 138.85 ($J_{^{119}\mathrm{Sn}}$ 539.2, $J_{^{117}\mathrm{Sn}}$ 515.2), 151.10; $\delta_{^{119}\mathrm{Sn}}$ −153.22. *E*-**18** was obtained in trace amount only, and showed the following ^{1}H NMR spectrum. δ_H 1.30 (3 H, d, *J* 6.52), 4.58 (1 H, ddq, *J* 6.40, 1.00, 6.52), 6.23 (1 H, dd, *J* 19.06, 6.40, $J_{^{119}\mathrm{Sn}}$ 76.30, $J_{^{117}\mathrm{Sn}}$ 73.06), 6.54 (1 H, dd, *J* 19.06, 1.00, $J_{^{119}\mathrm{Sn}}$ 49.78, $J_{^{117}\mathrm{Sn}}$ 47.54), 7.35 (9 H, m), 7.55 (6 H, m) and 7.78 (1 H, s, OOH).

3-*Methyl*-4-*triphenylstannyl*-1,2-*dioxolane* (**19**). This was formed in less than 5% yield; its ^{1}H NMR characteristics are given in Table 2.

Cyclohex-2-*enyl hydroperoxide* (**26**).[65] δ_H 1.56 (1 H, m), 1.72 (2 H, m), 1.87–2.10 (3 H, complex), 4.46 (1 H, m), 5.72 (1 H, dm, *J* 10.10, 1.75), 5.97 (1 H, dm, *J* 10.10, 1.34) and 8.20 (1 H, br, OOH); δ_C 18.40, 25.32, 26.39, 78.43, 124.12 and 134.32.

3-*Triethylsilylcyclohexen*-2-*yl hydroperoxide* (**28**). δ_H 0.57 (6 H, q, *J* 7.93), 0.89 (9 H, t, *J* 7.93), 1.55 (1 H, m), 1.71 (2 H, m), 1.92 (2 H, m), 2.05 (1 H, m), 4.46 (1 H, m), 5.94 (1 H, quint., *J* 2.05) and 7.75 (1 H, br, OOH); δ_C 2.34, 7.37, 19.19, 26.55, 27.89, 79.13, 132.38 and 144.69; $\delta_{^{29}\mathrm{Si}}$ 1.37; ν_{max}(neat)/cm^{-1} 3392, 2944, 2872, 1456, 1235, 729; *m*/*z* (70 eV) 210 (M^+ − 18, 5%), 195 (4), 181 (63), 153 (80), 75 (100).

Cyclohexen-2-yl trimethylstannyl peroxide (**38**), cyclohex-2-enyl tributylstannyl peroxide (**32**) and cyclohex-2-enyl triphenylstannyl peroxide (**40**) all gave the hydroperoxide **26** on silica gel. In the reaction mixture they were identified by the characteristic signals for the alkenic protons at δ 4.28, 4.25 and 4.50, respectively. For comparison, the tributylstannyl compound was prepared by the reaction of **26** with tributyltin methoxide, as a moisture-sensitive oil. δ_H 0.87 (9 H, t, *J* 7.30), 1.16 (6 H, t, *J* 8.39), 1.30 (6 H, m), 1.47–1.70 (9 H, complex), 1.90 (2 H, m), 1.98 (1 H, m), 4.25 (1 H, m), 5.72 (1 H, m) and 5.86 (1 H, m); δ_C 13.59, 15.22, 18.60, 25.46, 26.32, 27.14, 27.94, 78.05, 125.30 and 132.64; $\delta_{^{119}\mathrm{Sn}}$ 121.5.

The endoperoxides **39**, **33** and **41** all decomposed on silica gel as discussed in the text; their NMR characteristics are given in Table 2.

Reactions of PTAD.—General procedure. An equivalent of the allylic metallic compound was added to a solution of 0.5 g (2.85 mmol) of PTAD in CH_2Cl_2 under argon. When the colour of the PTAD had gone, any insoluble tin compound was filtered off and washed with solvent. The soluble component was chromatographed using CH_2Cl_2–ether (10:1, v:v), and products were purified by recrystallisation from CH_2Cl_2–pentane or by further chromatography. The allyl-2-metallotriazolidines **20**, **23**, **29**, **34**, **42** and **44** underwent hydrolysis on the column to give the corresponding protic compounds. The characteristics of all the products are given below.

4-*Phenyl*-1-*prop*-2-*enyl*-1,2,4,-*triazolidine*-3,5-*dione* (from **20**). M.p. 114–115 °C (lit.,[46] 116.5–117.5 °C); δ_H 4.17 (2 H, ddd, *J* 6.30, 1.10, 0.50), 5.30 (1 H, ddd, *J* 10.15, 2.53, 0.50), 5.34 (1 H, ddd, *J* 17.10, 2.53, 1.10), 5.83 (1 H, ddd, *J* 17.10, 10.15, 6.30), 7.34 (1 H, m), 7.47 (4 H, m) and 8.62 (1 H, br, NH); δ_C 49.36, 120.92, 125.51, 128.34, 129.17, 131.05, 130.14, 152.66 and 153.74 (C=O).

3-*Phenyl*-7-*trimethylstannyl*-1,3,5-*triazabicyclo*[3.3.0]*octane*-2,4-*dione* (**22**). M.p. 133–135 °C; δ_H 0.19 (9 H, s, $J_{^{119}\mathrm{Sn}}$ 55.12, $J_{^{117}\mathrm{Sn}}$ 52.72), 1.91 (1 H, tt, *J* 11.51, 7.51), 3.41 (2 H, dd, *J* 11.48, 12.63), 4.19 (dd, *J* 11.51, 7.51), 7.33 (1 H, m) and 7.45 (4 H, m). Values of δ_C and δ_{Sn} are given in the text. ν_{max}(Nujol)/cm^{-1} 1763 and 1698; *m*/*z* (70 eV) 381 (M^+, 13%) and 165 (100) (Found: C, 44.45; H, 5.1; N, 11.05. $C_{14}H_{19}N_3O_2Sn$ requires C, 44.25; H, 5.04; N, 11.06%).

1-(1-*Methylprop*-2-*enyl*)-4-*phenyl*-1,2,4-*triazolidine*-3,5-*dione* (from **23**). M.p. 98–100 °C (lit.,[46] 99–100 °C); δ_H 1.37 (3 H, 2 d, *J* 6.96, 6.86), 4.82 (1 H, m), 5.26 (1 H, d, *J* 10.38), 5.31 (1 H, d, *J* 17.35), 5.88 (1 H, ddd, *J* 17.35, 10.30, 6.90) and 8.60 (1 H, br, NH); δ_C 16.21, 54.26, 118.44 and 135.13 (vinyl), 125.46, 128.22, 129.10 and 131.15 (aromatic), 152.61 and 154.12 (C=O).

1-(1-*Methyl*-3-*triphenylstannylprop*-2-*enyl*)-4-*phenyl*-,1,2,4-*triazolidine*-3,5-*dione* (**24**) was formed in less than 5% yield. δ_H 1.22 (3 H, d, *J* 6.85), 4.47 (1 H, m), 6.52 (1 H, d, *J* 12.60, $J_{^{119}\mathrm{Sn}}$ 73.4, $J_{^{117}\mathrm{Sn}}$ 70.4), 6.81 (1 H, dd, *J* 12.60, 7.92, $J_{^{119}\mathrm{Sn}}$ 160.96, $J_{^{117}\mathrm{Sn}}$ 153.74).

6-*Methyl*-3-*phenyl*-7-*triphenylstannyl*-1,3,5-*triazabicyclo*-[3.3.0]*octane*-2,4-*dione* (**25**). This was obtained as a glass, m.p. 70–75 °C; a partial ^{1}H NMR spectrum is shown in Fig. 2. *trans*-**25**: δ_H 1.34 (3 H, d, *J* 6.96), 2.68 (1 H, ddd, *J* 13.20, 7.68, 6.80), 3.78 (1 H, dd, *J* 11.29, 13.20), 4.39 (1 H, dd, *J* 11.29, 7.68), 4.81 (1 H, dq, *J* 6.80, 6.96), 7.30–7.60 (20 H, complex). *cis*-**25**: δ_H 1.52 (3 H, d, *J* 6.20), 2.58 (1 H, ddd, *J* 12.40, 11.20, 7.65), 4.17 (1 H, dd, *J* 7.65, 10.25) and 7.32–7.58 (20 H, complex). Values of δ_C and δ_{Sn} are given in Table 3. ν_{max}(Nujol)/cm^{-1} 3052, 2925, 2851, 1765, 1705, 1071 and 725; *m*/*z* (70 eV) 581 (M^+, 7%), 350 (100) (Found: M^+, 581.2068. $C_{30}H_{27}N_3O_2Sn$ requires *M*, 581.2094).

1-*Cyclohex*-2-*enyl*-4-*phenyl*-1,2,4-*triazolidine*-3,5-*dione* (**27**). M.p. 168–171 °C (lit.,[46] 171–172 °C); δ_H 1.65 (1 H, m), 1.80 (2 H, m), 1.95 (1 H, m), 2.02 (2 H, m), 4.80 (1 H, m), 5.57 (1 H, dm, *J* 10.05, 2.24), 6.02 (1 H, dm, *J* 10.05, 2.37), 7.35 (1 H, m), 7.48 (4 H, m) and 8.50 (1 H, br, NH); δ_C 20.31, 24.34, 26.14, 52.59, 124.10 and 134.51 (vinyl), 125.42, 128.01, 129.03 and 131.35 (aromatic), 152.18 and 153.71 (C=O).

The triethylsilyl derivative **29** gave the corresponding protic compound **27** after separation on silica gel.

4-*Phenyl*-11-*triethylsilyl*-2,4,6-*triazatricyclo*[5,3,1,0^{2,6}]*undecane*-3,5-*dione* (**30**). Viscous oil. δ_H 0.71 (6 H, q, *J* 7.99), 1.00 (9 H, t, *J* 7.99), 1.42 (1 H, sept., *J* 2.25), 1.64 (2 H, m), 1.79 (2 H, m), 2.00 (2 H, m), 4.63 (2 H, t, *J* 4.21), 7.33 (1 H, m), 7.45 (4 H, m). Values for δ_C and δ_{Si} are given in Table 3. ν_{max}(neat)/cm^{-1} 2499, 2872, 1767, 1709, 1499, 1402, 729; *m*/*z* (70 eV) 371 (M^+, 5%), 342 (3), 292 (34), 262 (42), 115 (61) and 87 (100) (Found: M^+, 371.2045. $C_{20}H_{29}N_3O_2Si$ requires *M*, 371.2019).

4-*Phenyl*-1-(3-*triethylsilylcyclohex*-2-*enyl*)-1,2,4-*triazolidine*-3,5-*dione* (**31**). Viscous oil. δ_H 0.55 (6 H, q, *J* 7.98), 0.86 (9 H, t, *J* 7.98), 1.61 (2 H, m), 1.71 (2 H, m), 1.98 (2 H, m), 4.81 (1 H, m), 5.77 (1 H, d, *J* 1.68) and 7.45 (1 H, br, NH); δ_C 2.23, 7.33, 21.14, 26.03, 26.90, 53.60, 125.53, 128.07, 129.02 and 131.36 (aromatic), 132.37 and 145.22 (vinyl), 152.28 and 153.89 (C=O); ν_{max}(neat)/cm^{-1} 3168, 2944, 2864, 1763, 1698, 1497 and 729; *m*/*z* (70 eV) 371 (M^+, 3%), 342 (2), 292 (34), 262 (28), 115 (100) and 87 (96) (Found: M^+, 371.1998. $C_{20}H_{29}N_3O_2Si$ requires *M*, 371.2019).

The triorganostannyltriazolinediones **34**, **42** and **44** all gave the corresponding protic compound **27** during separation on silica gel.

4-*Phenyl*-11-*trimethylstannyl*-2,4,6-*triazatricyclo*[5.3.1.0^{2,6}]-*undecane*-3,5-*dione* (**43**). M.p. 236–238 °C; δ_H 0.24 (9 H, s, $J_{^{119}Sn}$ 54.28, $J_{^{117}Sn}$ 52.0), 1.54 (2 H, m), 1.62 (1 H, m, J_{Sn} 48), 1.76 (1 H, m), 1.90 (1 H, m), 2.00 (2 H, m), 4.66 (2 H, t, *J* 4.50), 7.34 (1 H, m) and 7.45 (4 H, m). Values for δ_C and δ_{Sn} are given in Table 3. ν_{max}(Nujol)/cm^{-1} 2952, 2920, 2865, 1760 and 1705; *m*/*z* (70 eV) 421 (M$^+$, 10%), 340 (23) and 165 (100).

4-*Phenyl*-11-*tributylstannyl*-2,4,6-*triazatricyclo*[5.3.1.0^{2,6}]*undecane*-3,5-*dione* (**35**). M.p. 52 °C; δ_H 0.90 (9 H, t, *J* 7.27), 0.98 (6 H, t, *J* 8.46), 1.32 (6 H, m), 1.44–1.56 (8 H, complex), 1.65 (1 H, sept., *J* 2.24), 1.75 (1 H, m), 1.86 (1 H, m), 2.04 (2 H, m), 4.63 (2 H, t, *J* 4.43), 7.33 (1 H, m) and 7.46 (4 H, m). Values for δ_C and δ_{Sn} are given in Table 3. ν_{max}(neat)/cm^{-1} 2950, 2922, 2866, 2859, 1759 and 1706; *m*/*z* (70 eV) 547 (M$^+$, 3%), 490 (25) and 81 (100) (Found: M$^+$, 547.2230. $C_{26}H_{41}N_3O_2Sn$ requires *M*, 547.2211).

4-*Phenyl*-11-*triphenylstannyl*-2,4,6-*triazatricyclo*[5.3.1.0^{2,6}]-*undecane*-3,5-*dione* (**45**). M.p. 235–237 °C; δ_H 1.52 (1 H, m), 1.70 (2 H, m), 1.82 (1 H, m), 1.94 (2 H, m), 2.38 (1 H, m, $J_{^{119}Sn}$ 45.27, $J_{^{117}Sn}$ 43.80), 4.93 (2 H, t, *J* 4.42) and 7.30–7.60 (20 H, complex). Values of δ_C and δ_{Sn} are given in Table 3. ν_{max}(Nujol)/cm^{-1} 2925, 2852, 1765, 1705, 1454, 1374, 1071 and 727; *m*/*z* (70 eV) 452 (M$^+$ − 155), 348 (100) and 81 (96) (Found: C, 63.25; H, 4.9; N, 6.85. $C_{32}H_{29}N_3O_2Sn$ requires C, 63.37; H, 4.82; N, 6.94%).

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