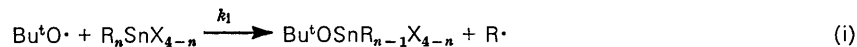


Homolytic Organometallic Reactions. Part XI.¹ The Reactions of *t*-Butoxyl Radicals and of Ketone Triplets with Organotin Compounds

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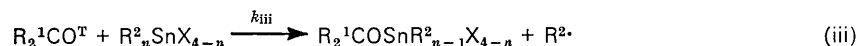
Whereas *t*-butoxyl radicals react with tetra-alkyltins at the α -hydrogen centres, the presence of electronegative ligands X in the compounds $R_n\text{SnX}_{4-n}$ (X = halide or carboxylate; $n = 1-3$) directs attack to the tin atom [equation (i)]. If the *t*-butoxyl radical is generated by photolysis of di-*t*-butyl peroxide, the displaced radical R \cdot



can be observed by e.s.r. spectroscopy. If the *t*-butoxyl radical is derived from *t*-butyl hypochlorite, a chain reaction is established with reactions (i) and (ii) as the propagating steps. For tripropyltin chloride, $k_1 = 10^{6.58} \exp(-1.130/\theta) \text{ l mol}^{-1} \text{ s}^{-1}$ ($\theta = 2.303RT$), and $k_1(30^\circ) = 1.1 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$. Ketone triplets similarly bring



about an $S_{\text{H}}2$ reaction at the tin centre [equation (iii)]. For tripropyltin chloride and acetophenone, $k_{\text{iii}} = 4.0 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$, and for *p*-methylacetophenone, $k_{\text{iii}} = 2.2 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ at room temperature, both



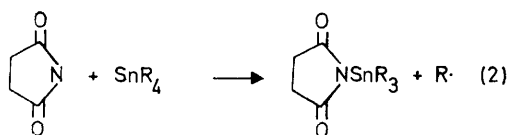
with a quantum yield of 0.13.

BIMOLECULAR homolytic displacement of an alkyl radical from a metal centre (equation (1)) has been



established for organic derivatives of metals of Groups I-III and V, where the metal has co-ordination number 1-3.² Displacement at a centre with co-ordination number 4 or higher is relatively rare. For example, whereas trialkylboranes are reactive by equation (1) towards a variety of reagents X, no such reaction has yet been discovered with their four-co-ordinate amine complexes. In Group IV, there is no simple established example of an $S_{\text{H}}2$ reaction at a saturated carbon centre, nor any example of displacement of an alkyl group from four-co-ordinate silicon or germanium.[†]

Razuvaev and his co-workers have suggested that the products of the pyrolysis of organic peroxides in the presence of tetra-alkyltins imply the $S_{\text{H}}2$ reactions of alkyl and acyloxyl radicals at the metal centres,⁴ but alternative explanations cannot be excluded. The best previous evidence for homolytic displacement of an



alkyl radical from a tin centre appears to be the process of succinimidydealkylation [equation (2)] which is involved in the reaction between *N*-halogenosuccinimides and tetra-alkyltins.⁵

[†] There are, however, well-established examples of the cleavage of an Si-Si or Sn-Sn bond by an $S_{\text{H}}2$ process.³

¹ Part X, A. G. Davies and J. C. Scaiano, *J.C.S. Perkin II*, 1972, 2234.

² A. G. Davies and B. P. Roberts, *Accounts Chem. Res.*, 1972, 5, 387.

We now report that, whereas *t*-butoxyl radicals or ketone triplets react at the hydrogen centres in tetra-alkyltins, the presence of electronegative ligands X, such as halide or carboxylate, in the compounds $R_n\text{SnX}_{4-n}$ ($n = 1$ or 2), directs attack to the tin centre, and homolytic dealkylation can be observed.

RESULTS

t-Butoxyl Radicals from Photolysis of Di-*t*-butyl Peroxide.—When a mixture of di-*t*-butyl peroxide and tetraethyltin is irradiated with u.v. light in the cavity of an e.s.r. spectrometer, the spectrum of the radical $\text{Et}_3\text{Sn}\dot{\text{C}}\text{HCH}_3$ can be observed. Similarly, tributyltin propoxide shows the presence of the radical $\text{Bu}_3\text{SnO}\dot{\text{C}}\text{H}\text{Et}$. Alkyltin halides or carboxylates, $R_n\text{SnX}_{4-n}$ ($n = 2$ or 3), on the other hand, gave a strong spectrum of the corresponding radical R \cdot . When the peroxide was absent a relatively weak spectrum of the radical was obtained; for example with tripropyltin chloride, the intensity of the spectrum was enhanced about five times by the presence of the peroxide, corresponding to a 25-fold increase in the rate of formation of Pr \cdot , while the rate of direct photodecomposition should have decreased, due to decreased absorption by the organotin compound in the mixture with the peroxide. When $n = 1$ (e.g. with BuSnCl_3), the effect of the peroxide on the intensity of the spectrum was not convincing. The qualitative results are summarised in Table 1.

Some similar experiments were also carried out with derivatives of silicon, germanium, and lead. Alkylsilanes and alkylgermanes underwent hydrogen abstraction (see the last two entries in Table 1). A variety of organolead compounds all decomposed photolytically, giving metallic lead and other solid deposits.

³ E.g. silicon, A. Hosimi and H. Sakurai, *J. Amer. Chem. Soc.*, 1972, 94, 1384; *Chem. Letters*, 1972, 193; tin, W. P. Neumann, K. Rüksamen, and R. Sommer, *Chem. Ber.*, 1967, 100, 1063.

⁴ E.g. N. S. Vyazankin, G. A. Razuvaev, and T. N. Brevnova, *Zhur. obshchei Khim.*, 1965, 35, 2033.

⁵ A. G. Davies, B. P. Roberts, and J. M. Smith, *J.C.S. Perkin II*, 1972, 2221.

E.s.r. parameters for some of the metalloalkyl radicals are listed in Table 2.

TABLE 1

Photolysis of di-*t*-butyl peroxide in the presence of organotin compounds

R _n SnX _{4-n}	Solvent ^a	Temp. (°C)	Radical observed ^b
Me ₃ SnCl	PhMe	-30	None
Et ₃ Sn	PhMe	-78 to +67	Et ₃ SnĊHCH ₃
Et ₃ SnOCOH ^c	PhH, C ₅ H ₁₀	-20 to 0	Et·
Et ₃ SnOCOMe	PhH	-10 to +10	Et·
Et ₃ SnOCOFC ₃	PhMe	-65 to +40	Et·
Et ₂ SnCl ₂	PhMe, C ₅ H ₆	-70 to 0	Et·
Pr ₄ Sn	PhMe	-80 to +70	Pr ₃ SnĊHEt
Pr ₃ SnCl	PhMe, C ₅ H ₁₀	-100 to +40	Pr·
Bu ₃ SnF	PhMe	-30	None ^d
Bu ₃ SnCl	PhMe	-60 to -30	Bu·
Bu ₃ SnBr ^e	PhMe	-20	Bu·
Bu ₃ SnOPr	PhMe	-50	Bu ₃ SnOĊHEt
Bu ₃ SnOCOCCl ₃	PhMe	-90 to -30	Bu·
Bu ₂ SnCl ₂	PhMe	-30 to +30	Bu·
Bu ₂ Sn(OCOMe) ₂	PhMe	-80 to -40	(Bu·)
BuSnCl ₃	PhMe	-30	(Bu·)
SnCl ₄ ^f	C ₅ H ₁₀	-50 to +30	Me·
Et ₂ SiCl	PhMe	-50 to +30	Et ₂ Si(Cl)ĊHCH ₃
Et ₂ GeCl	PhMe	-50	Et ₂ Ge(Cl)ĊHCH ₃

^a C₃H₆ = Cyclopropane; C₅H₁₀ = cyclopentane. ^b Radicals in parentheses indicate weak signals. ^c A precipitate separated during irradiation. ^d Probably because tributyltin fluoride has a low solubility. ^e Significant photodecomposition occurred in the absence of the peroxide. ^f A. G. Davies, B. P. Roberts, and J. C. Scaiano, *J. Organometallic Chem.*, 1972, **42**, C27.

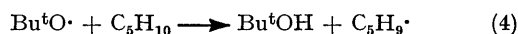
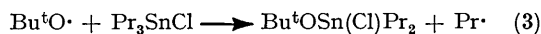
TABLE 2

E.s.r. parameters of metalloalkyl radicals

Radical	Temp. (°C)	Hyperfine coupling (G)	
		a(α-H)	a(β-H)
Et ₃ SnĊHCH ₃ ^a	-9	20.1	25.6
Et ₂ Si(Cl)ĊHCH ₃ ^b	-20	ca. 20	ca. 25 ^c
Pr ₃ SnĊHCH ₂ CH ₃ ^a	-23	19.8	25.6
Bu ₃ SnOĊHCH ₂ CH ₃ ^a	-50	13.2	20.6

^a In toluene. ^b Et₂SiCl in neat Bu₂tO₂. ^c a(Cl) ca. 3.2 G.

The kinetics of the reaction of *t*-butoxyl radicals with tripropyltin chloride were measured by causing reaction (3) to compete with the abstraction of hydrogen from cyclopentane [equation (4)], which was used as solvent.



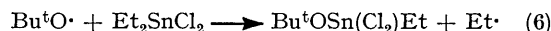
The technique, and the assumptions involved, have been discussed previously.⁶ The relative concentrations of the propyl and cyclopentyl radicals were determined from the intensities of the e.s.r. spectra, and the ratio of the rate constants of reactions (3) and (4) was derived from expression (5).

$$\frac{k_3}{k_4} = \frac{[\text{Pr}\cdot][\text{C}_5\text{H}_{10}]}{[\text{C}_5\text{H}_9\cdot][\text{Pr}_3\text{SnCl}]} \quad (5)$$

The system was examined from -92 to +15°, and the results gave a good Arrhenius plot (Figure 1) from which we obtain $\log(k_3/k_4) = (-2.12 \pm 0.20) + (4.05 \pm 0.20)/\theta$, where $\theta = 2.303RT$ kcal mol⁻¹, whence $\log(k_3/1 \text{ mol}^{-1} \text{ s}^{-1}) = 6.88 - 1.130/\theta$ and, at 10°, $k_3 = 1.0 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$.

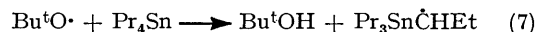
A similar series of experiments was also attempted with diethyltin dichloride [equation (6)], but the system could

not be examined below -20° because of solubility problems, and the fraction of substrate photodecomposition, which also gives ethyl radicals, was significant.



The temperature dependence of the reaction is probably affected by a number of factors, but, at 10°, if the photodecomposition is neglected, $k_6(10^\circ) = 1 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ and, for the activation energies of the two reactions, $E_6 < E_4$.

For comparison, the kinetics of reaction (7) were also



studied. The Arrhenius plot which was obtained is shown in Figure 1, giving $\log k_7/k_4 = (0.46 \pm 0.11) + (0.44 \pm 0.12)/\theta$, whence $\log(k_7/1 \text{ mol}^{-1} \text{ s}^{-1}) = 9.46 - 4.760/\theta$.

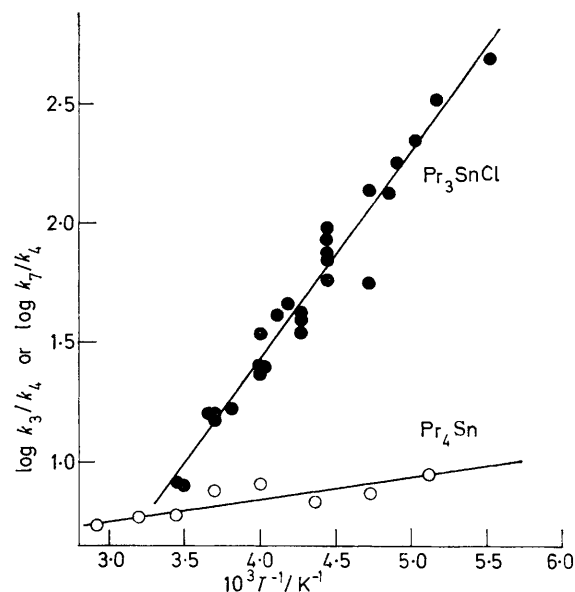


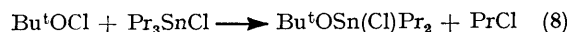
FIGURE 1 Arrhenius plot of $\log k_3/k_4$ (for Pr₃SnCl) and of $\log k_7/k_4$ (for Pr₄Sn) against reciprocal temperature

If the reactivity at hydrogen is similar in Pr₃SnCl and Pr₄Sn, it is clear that reaction at the tin centre in tripropyltin chloride should be favoured at low temperatures.

A complicating factor in the e.s.r. experiments was the occurrence, under some conditions, of a broad singlet (g ca. 1.99) accompanying the multiplet of the alkyl radicals. This signal was absent for the first few minutes' irradiation of a carefully purified organotin compound, but it was present in an unpurified sample, or after prolonged irradiation. A series of experiments under different initial conditions showed that the above kinetic results were independent of this singlet. The dependence of the concentration of the radical Pr·, and of the species giving rise to the singlet, derived from tripropyltin chloride, was determined at different light intensities; the results are shown in Figure 2. Both radicals disappear in bimolecular processes, supporting the conclusion that the species which gives rise to the singlet is not an intermediate in the formation of the propyl radical.

⁶ A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc. (B)*, 1971, 1823.

t-Butoxyl Radicals from *t*-Butyl Hypochlorite.—A spontaneous reaction occurs between *t*-butyl hypochlorite and tripropyltin chloride in carbon tetrachloride at room temperature, according to equation (8).



The n.m.r. signal of the *t*-butyl hypochlorite at τ 8.72 is replaced by one at τ 8.80, and the triplet of the α -methylene group of propyl chloride appears at τ 6.56. After 4 h, the yield of propyl chloride is *ca.* 55%, extrapolating at infinite

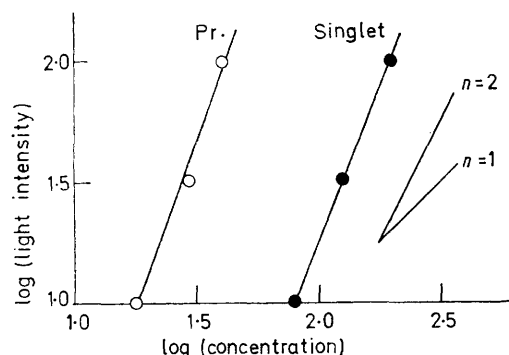
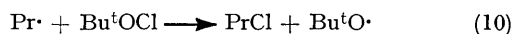
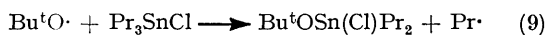


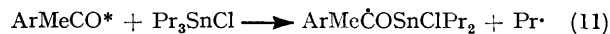
FIGURE 2 Logarithmic plot of light intensity against concentration of propyl radicals, and of the unidentified species giving rise to the e.s.r. singlet; both units arbitrary

time to 70% or better. The formation of propyl chloride was verified by g.l.c., and the presence of a compound Pr_2SnClX was confirmed by causing it to react with bipyridyl when Pr_2SnCl_2 , bipy was isolated.⁷

The n.m.r. spectrum also showed that another product was present in about half the concentration of that of the propyl chloride. The spectrum [τ 6.42 (*t*), *J ca.* 5 Hz] suggested that this compound might contain a methyleneoxy-group, but it appeared not to be *t*-butyl propyl ether. Galvinoxyl (0.25 mol %) inhibited the formation of the propyl chloride, but not of the unidentified compound. It seems that a parallel heterolytic reaction accompanies the homolytic formation of propyl chloride. In view of the e.s.r. experiments described above, the most probable mechanism appears to be a homolytic chain reaction with the propagation steps shown in equations (9) and (10).



Ketone Triplets.—When a mixture of acetophenone or *p*-methylacetophenone and tripropyltin chloride in benzene, toluene, or cyclopentane, is irradiated in the cavity of an e.s.r. spectrometer, the spectrum of the propyl radical, superimposed on a second spectrum, can be observed. This second spectrum is very similar to that of the appropriate ketyl radical, $\text{Ar}\dot{\text{C}}(\text{OH})\text{Me}$, but there are distinct differences in detail. A complete analysis was not possible because the signals of the two species overlapped. By analogy with the reaction of ketone triplets with organoboranes,¹ we assume that this radical is the species $\text{ArMe}\dot{\text{C}}\text{OSnClPr}_2$, which is formed by reaction (11).



⁷ A. G. Davies and P. G. Harrison, *J. Chem. Soc. (C)*, 1967, 298.

No radicals were observed when acetone was used in place of the aromatic ketones, but the presence of acetone triplets in the system was confirmed by the isomerization of *cis*-piperylene.

Quantum yields in the reactions involving acetophenone and *p*-methylacetophenone were determined using the *cis-trans* isomerization of piperylene as an actinometer.^{1,8} This technique measures triplet input rather than radiation dose. For an 0.3M solution of tripropyltin chloride in benzene at room temperature, the quantum yield for ketone removal is equal for both ketones.

The rate of reaction (11) was determined for both ketones from Stern-Volmer plots, studying the effect of increasing concentrations of *cis*-piperylene on the quantum yield of the reaction in benzene, at radiation dose rates of *ca.* 2.6×10^{-8} einstein $\text{l}^{-1} \text{s}^{-1}$. For acetophenone, $k_{11} = 4.0 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$, and for *p*-methylacetophenone, $k_{11} = 2.2 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$.

The yield of isomerized piperylene (0.2M-*cis*-isomer initially) after a small correction for the value of k_{11} , was independent of the presence of tripropyltin chloride (0.2M) showing that the organotin compound does not absorb any significant fraction of the light.

A mixture of acetophenone and tripropyltin chloride was irradiated on a larger scale for 9 h, when the products were hydrolysed and examined by g.l.c. The gas phase over the solution contained propane and propene in the ratio *ca.* 50 : 1. In the liquid phase, 2-phenylpentan-2-ol (15–20% yield), and no 1-phenylethanol, were detected.

DISCUSSION

Rate constants for the reaction of *t*-butoxyl radicals and of ketone triplets with organotin compounds are collected in Table 3, from which the effect of the chlorine in diverting attack from hydrogen to the tin centre is apparent. For comparison, the rate constants for the reaction at the boron centre in tri-*n*-butylborane by the *t*-butoxyl radical is $3 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ (with zero activation energy) and, by the acetophenone triplet, is *ca.* $10^8 \text{ l mol}^{-1} \text{ s}^{-1}$.

TABLE 3

Reaction of *t*-butoxyl radicals and of ketone triplets with organotin compounds

Reagent	$\text{R}_n\text{SnX}_{4-n}$	Reaction site	Rate ^a constant	Ref.
$\text{Bu}^t\text{O} \cdot$	Pr_3Sn	H(α -C)	3×10^8	<i>b</i>
$\text{Bu}^t\text{O} \cdot$	Pr_3SnCl	Sn	1×10^6	<i>b</i>
$\text{Bu}^t\text{O} \cdot$	Et_2SnCl_2	Sn	1×10^6	<i>b</i>
$\text{Ph}_2\text{CO}^{\text{T}}$	Bu_3Sn	H(α -C)	7×10^5	<i>c</i>
PhMeCO^{T}	Bu_3SnCl	Sn	4×10^8	<i>b</i>
$(p\text{-MeC}_6\text{H}_4)\text{MeCO}^{\text{T}}$	Pr_3SnCl	Sn	2.2×10^8	<i>b</i>
$\text{Me}_2\text{CO}^{\text{T}}$	Bu_3SnH	H(Sn)	2×10^8	<i>d</i>
$\text{Ph}_2\text{CO}^{\text{T}}$	Bu_3SnH	H(Sn)	4.7×10^7	<i>c</i>

^a $1 \text{ mol}^{-1} \text{ s}^{-1}$ at *ca.* 10^5 . ^b This work. ^c D. R. G. Brimage, R. S. Davidson, and P. F. Lambeth, *J. Chem. Soc. (C)*, 1971, 1241. The original value has been recalculated using k_0 (piperylene) = $2.4 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ (H. Lutz and L. Lindqvist, *Chem. Comm.*, 1971, 493). ^d P. J. Wagner, *J. Amer. Chem. Soc.*, 1967, **89**, 2503.

Alkoxyl radicals and ketone triplets, in common with other electronegative radical species, behave as electrophiles when they react at benzylic hydrogen centres, in

⁸ G. S. Hammond and A. A. Lamola, *J. Chem. Phys.*, 1965, **43**, 2129.

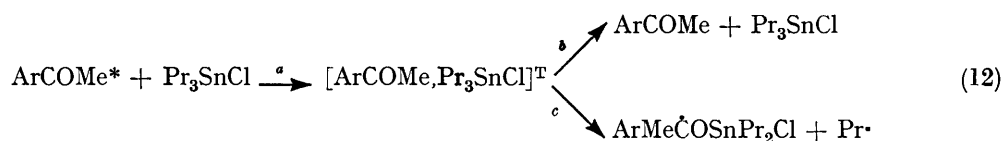
that electron release to the reagent by substituents in the substrate stabilise the polar form (e.g.

$\text{Bu}^t\text{O}^- \dot{\text{H}} \overset{+}{\text{C}}\text{H}_2\text{Ar}$) which makes a significant contribution to the resonance hybrid in the transition state. Electronegative substituents (X) at a tin centre might therefore be expected to reduce the reactivity by destabilising the

canonical form $\text{Bu}^t\text{O}^- \text{R}_2\overset{+}{\text{S}}\text{nX} \dot{\text{R}}$. Clearly, if this effect is indeed important, it must be over-ridden by some opposing effect.

This second effect is probably connected with the Lewis base character of the reagent as it associates with the metal centre to form the transition state. This process involves an increase in the effective co-ordination number of the metal, which is usually facilitated by the presence of electronegative ligands. The difference between the reactivity of tetra-alkyltins and trialkyltin halides towards alkoxy radicals or ketone triplets may then be compared with the fact that tetra-alkyltins do not form pyridine complexes, but trimethyltin chloride does give an isolable five-co-ordinate complex, in which the two electronegative substituents occupy axial positions in a trigonal tripyramid.⁹

The $\text{S}_{\text{R}}2$ reactions of carbonyl triplets with organotin compounds show the same characteristics as the reactions with organoboranes, in that the rate constants are very large, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ triplets show a similar reactivity, and quantum yields are moderate. From the life-time of the triplets in benzene solution, it appears that *all* the triplets are quenched by the organotin compounds, which implies that it is acting as both a chemical and a physical quencher. These characteristics are usually interpreted^{1,10} in terms of the irreversible formation of a triplet exciplex which can revert to the reagents or proceed to products [reaction (12)], and the experimental quantum yield of 0.13 can be taken to mean that $k_{12c}/(k_{12c} + k_{12b}) = 0.13$.



The large propane:propene ratio observed in the reaction of acetophenone triplets seems to suggest that hydrogen abstraction is one of the main routes for removal of the propyl radical from the system.

EXPERIMENTAL

Reagents.—The purity of the organotin compounds was checked by m.p., n.m.r. spectroscopy, or g.l.c., as appropriate. *cis*-Piperylene (Fluka) was shown by g.l.c. to be free from isomers. AnalaR solvents were used throughout, and all the experiments were carried out under nitrogen.

E.s.v. Experiments.—Spectra were recorded on a Varian

E4 spectrometer fitted with a Mazda 1000 W ME/D high pressure mercury arc and a standard variable-temperature unit. Radiation doses were *ca.* 4×10^{-4} einstein $\text{l}^{-1} \text{s}^{-1}$.

The light intensity was varied with metal screens which were calibrated using a Unicam SP 1800 spectrometer.

Quantum Yields.—Irradiations were carried out in a 'merry-go-round' immersed in water and fitted with a Hanovia 125 W medium pressure mercury arc enclosed in a quartz housing which was cooled by the forced circulation of water. The temperature was maintained at $28 \pm 1^\circ$. Samples were contained in matched Pyrex tubes. The concentration of the ketone after irradiation was determined by g.l.c. [2 m column of Apiezon L on Chromosorb P (15:85) at 190 – 220°], using n-dodecane as internal standard.

The triplet input was determined using the *cis-trans*-isomerization of piperylene as an actinometer, with the concentration of the ketone the same as in the samples. The initial concentrations of *cis*-piperylene were in the range 0.2–0.8M, which should quench all the triplets. The efficiency of the *cis-trans*-isomerization was taken to be 0.55, and the conversion was kept low so that quenching by the *trans*-isomer could be neglected.

Preparative Photochemical Experiments.—The light source was the same as in the other experiments, but the irradiations were carried out at a shorter range, and the dose rate was *ca.* 3×10^{-5} einstein $\text{l}^{-1} \text{s}^{-1}$.

Acetophenone (0.1 mmol) and tripropyltin chloride (0.7 mmol) in benzene (3 ml) was irradiated for 9 h. The gas phase over the solution was examined by g.l.c. for light hydrocarbons. The solution was hydrolysed with acid, and examined by g.l.c.

Experiments with *t*-Butyl Hypochlorite.—Tripropyltin chloride (0.9 mmol) and *t*-butyl hypochlorite (0.35 mmol) was caused to react at 35° in carbon tetrachloride (0.4 ml) containing benzene (20 μl) as an internal n.m.r. standard. The course of the reaction was followed by n.m.r. spectroscopy. Similar experiments were carried out in the presence of galvinoxyl (0.25 mol % on *t*-butyl hypochlorite).

The presence of propyl chloride in the product was confirmed by g.l.c. Treatment of the reaction products

with bipyridyl led to the precipitation of Pr_2SnCl_2 , bipy, which was identified by comparison with authentic sample.

We are grateful to Dr. B. P. Roberts for discussions, and to the S.R.C., the Royal Society, and the Central Research Fund of London University, for support.

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⁹ I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, 1963, 1519.

¹⁰ S. G. Cohen and N. M. Stein, *J. Amer. Chem. Soc.*, 1971, **93**, 6542 and references therein; R. S. Davidson and P. F. Lambeth, *Chem. Comm.*, 1957, 1265.