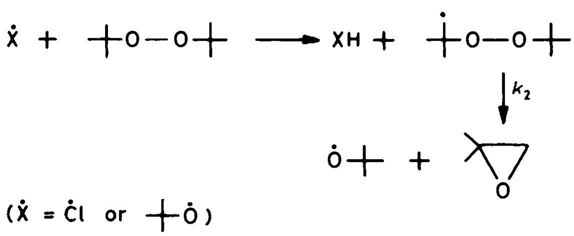
Rate Constants for the Formation of Oxiranes by γ-Scission in Secondary β-t-Butylperoxyalkyl Radicals

A. J. Bloodworth,* J. L. Courtneidge, and Alwyn G. Davies
Christopher Ingold Laboratories, Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ

Rate constants for the title reactions have been determined from the ratios of oxirane to peroxide obtained in the reductions of β-bromoalkyl t-butyl peroxides with tributyltin hydride. At *ca.* 298 K the rate constants are 0.32, 1.12, 1.96, 2.0, and 6.2 × 10^6 s^{-1} for β-t-butylperoxy derivatives of trinorbornan-2-yl (*exo*) cyclohexyl, 1-methylpropyl, cyclopentyl, and 1-ethylbutyl, respectively. The results are discussed in terms of steric and electronic effects in the transition state leading to ring closure of the radicals.

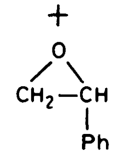
The γ-scission of β-peroxyalkyl radicals [equation (1)] is the key step in the formation of oxiranes in the thermal or photolytic decomposition of dialkyl peroxides,[1,2] in the autoxidation of alkenes,[3] and in the cool-flame combustion of hydrocarbons.[4,5] This process appears to have been first proposed [1] to account for the formation of isobutene oxide during the thermal or photochemical decomposition of di-t-butyl peroxide alone or in the presence of hydrogen chloride [equation (2)].


(1)


(2)

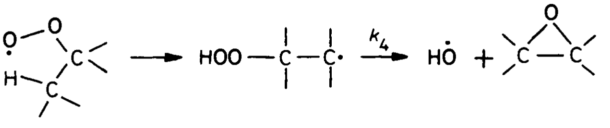
In the gas phase at 27—130 mmHg pressure and 130—160 °C, the yield is only 1—2%,[2] but the pure liquid peroxide at 110 °C gives up to 35% of the oxirane.[2] The activation energy was estimated to be between 10 and 16 kcal mol^{-1}, and the pre-exponential factor to be $10^{11.5}$ s^{-1}, which would be equivalent to a value of k_2 between 10^4 and 0.5 s^{-1} at 300 K.

In 1958, Mayo and his co-workers reported a thorough study of the autoxidation of alkenes in the liquid phase.[3] Styrene gave a maximum of 27% of the epoxide at 1 mmHg of oxygen, and the rate constant k_3 for the ring closure [equation (3)] was estimated to be approximately 2 × 10^3 s^{-1} at 283 K.[3a]


(3)

α-Methylstyrene underwent ring closure more rapidly giving a 40% yield of epoxide at 6 mmHg of oxygen,[3b] and 2,4,4-trimethylpent-1-ene, which does not undergo competitive homopolymerization, gave 43—54% of epoxide over the range 1—120 mmHg of oxygen.[3d]

In the autoxidation or cool-flame combustion of alkanes, oxiranes are believed to be formed by intramolecular 1,4-shift of hydrogen, followed by γ-scission of the resulting peroxyalkyl radical [equation (4)],[4] and Fish argued that the rate constant, k_4, for the ring closure of the 2-hydroperoxyethyl radical might be expected to be about 4 × 10^{-2} s^{-1} at 300 K.[5]


(4)

The availability of primary β-bromoalkyl peroxides *via* the products of peroxymercuriation of alkenes [equation (5)] [6a] provided a cleaner route to the β-peroxyalkyl radicals, and made it possible to measure the rates of some of the ring-closure reactions by a method based on the analysis, by g.l.c. or n.m.r. spectroscopy, of the products from competitive reactions involving tributyl- or triphenyl-tin hydride.[7]

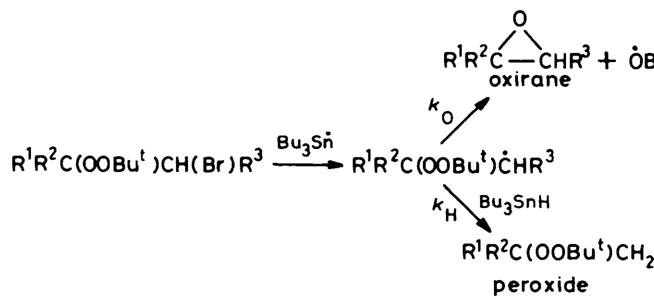
$$R^1R^2C{=}CHR^3 \xrightarrow[HgX_2]{Bu^tOOH} R^1R^2C(OOBu^t)CH(HgX)R^3 \xrightarrow{Br_2} R^1R^2C(OOBu^t)CH(Br)R^3 \quad (5)$$

We describe here an extension of these studies, by an improved technique, to a number of secondary β-bromoalkyl peroxides which have since become available by reaction (5).[6b] The results consolidate and amplify those obtained previously,[7] and provide a more complete picture of the factors influencing the ring-closure reactions.

Results

The method used was basically the same as that used previously [7] to determine rate constants for γ-scission in primary β-t-butylperoxyalkyl radicals: β-bromoalkyl t-butyl peroxides were caused to react with tributyltin hydride and the products were analysed for oxirane and alkyl t-butyl peroxide.

The reaction proceeds according to equation (6), so that the γ-scission, or intramolecular homolytic substitution at oxygen, competes with reduction of the radical by the tin hydride. The rate expressions for the competing processes are shown in equations (7) and (8), and integration over the time (t) of the reaction leads to expression (9).



(6)

$$\mathrm{d[oxirane]/d}t = k_\mathrm{O}\,[\mathrm{R^1R^2C(OOBu^t)\dot{C}HR^3}] \qquad (7)$$

$$\mathrm{d[peroxide]/d}t = k_\mathrm{H}\,[\mathrm{R^1R^2C(OOBu^t)\dot{C}HR^3}][\mathrm{Bu_3SnH}] \qquad (8)$$

$$\frac{\text{Yield of oxirane (mol)}}{\text{Yield of peroxide (mol)}} = \frac{k_\mathrm{O}}{k_\mathrm{H}\int_0^t [\mathrm{Bu_3SnH}]\mathrm{d}t} \qquad (9)$$

Since the ratios of the initial concentrations of hydride and bromoperoxide were generally in the range 3 : 1 to 8 : 1, the approximation was made that the tributyltin hydride concentration remained constant and equal to that obtaining at half reaction, $[\mathrm{Bu_3SnH}]_{\frac{1}{2}}$. More sophisticated mathematical treatment [7b] of the data did not give significantly different results. The expression for the ratio of the rate constants thus reduced to that shown in equation (10).

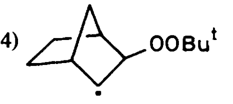
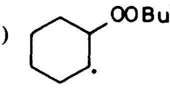
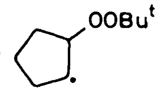
$$\frac{k_\mathrm{O}}{k_\mathrm{H}} = \frac{\text{Yield of oxirane (mol)}}{\text{Yield of peroxide (mol)}} \times [\mathrm{Bu_3SnH}]_{\frac{1}{2}} \qquad (10)$$

In our previous work we used 60 MHz ^{1}H n.m.r. spectroscopy for following the reduction with triphenyltin hydride,[7b] but the resolution of the signals with tributyltin hydride was unsatisfactory, and the reactions were followed by g.l.c.[7a] The resolution and sensitivity provided by Fourier transform n.m.r. spectroscopy at 200 MHz, however, is sufficient to determine the low concentrations of peroxide often obtained, and this is the technique we have used in the present work. By carrying out the reactions in an n.m.r. tube, manipulations of the reaction mixtures, with the risk of material losses, are avoided. The inclusion of an internal standard enabled absolute yields to be determined. The reliability of the method was checked by measuring the peak areas for a known mixture of composition similar to that obtained in one of the reactions.

It has been shown that the rate constant (k_H) for the abstraction of hydrogen by alkyl radicals from tributyltin hydride is approximately the same for representative primary, secondary, and tertiary alkyls.[8,9] The original determinations,[8] which were carried out by the rotating sector method, afforded a value for k_H of about 1×10^6 dm^3 mol^{-1} s^{-1} at 298 K, but more reliable measurements using laser flash photolysis have now indicated that this value should be doubled.[9] If it is assumed that the same rate constant is appropriate for the reductions of our β-t-butylperoxyalkyl radicals, then it is possible to calculate absolute rate constants (k_O) for γ-scission by using equation (10).

The results obtained are shown in Table 1, which, for comparison, includes our earlier results [7] for primary β-t-butylperoxyalkyl radicals; the absolute values of k_O for the latter species have been recalculated using the new value of k_H.

Table 1. Rate constant data for γ-scission in β-t-butylperoxyalkyl radicals at *ca.* 298 K

Radical	$k_\mathrm{o}/k_\mathrm{H}$ mol dm^{-3}	k_o/s^{-1} [a]	k_o(rel) [b]
(1) $\mathrm{CH_2(OOBu^t)\dot{C}H_2}$	0.002 [c]	4×10^3	1
(2) $\mathrm{MeCH(OOBu^t)\dot{C}H_2}$	0.04 [c]	8×10^4	20
(3) $\mathrm{Me_2C(OOBu^t)\dot{C}H_2}$	0.7 [c]	1.4×10^6	350
(4) 	0.16	3.2×10^5	80
(5) 	0.56	1.12×10^6	280
(6) $\mathrm{MeCH(OOBu^t)\dot{C}HMe}$	0.98	1.96×10^6	490
(7) 	1.0	2.0×10^6	500
(8) $\mathrm{EtCH(OOBu^t)\dot{C}HEt}$	3.1	6.2×10^6	1 550

[a] Calculated by assuming $k_\mathrm{H} = 2 \times 10^6$ dm^3 mol^{-1} s^{-1} (ref. 9). [b] k_O divided by rate constant for γ-scission in $\mathrm{CH_2(OOBu^t)\dot{C}H_2}$. [c] From ref. 7.

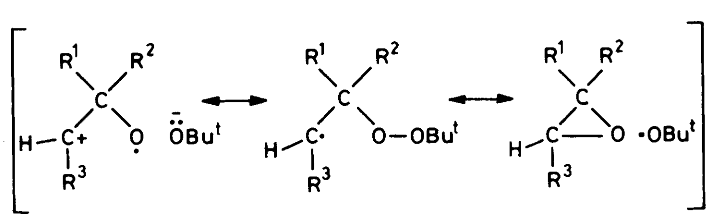
Discussion

Although the general mechanism of the reaction of alkyl bromides with tributyltin hydride is well established,[10] our results provide an independent stereochemical check that it applies also to our β-bromoalkyl t-butyl peroxides. Thus both diastereoisomers of each bromoperoxide, RCH(OOBuᵗ)CH(Br)R, were studied separately, and both isomers of each pair gave rise to the same product distribution (see Table 3). Furthermore, the same ratios of *trans*- to *cis*-oxiranes were obtained from both diastereoisomers for each of the two acyclic bromoperoxides ($\mathrm{R_2 = Me_2}$ or $\mathrm{Et_2}$). These observations are all consistent with the generation of intermediate β-t-butylperoxyalkyl radicals [equation (6)].

Our rate constants (Table 1) together with similar data obtained by Porter *et al.*[11,12] for radicals derived from cyclic peroxides (Table 2) provide a firm basis for comment upon the influence of structure on rates of intramolecular homolytic substitution at oxygen (γ-scission) in β-peroxyalkyl radicals.

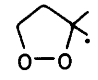
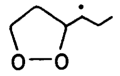
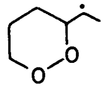
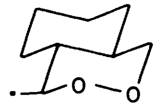
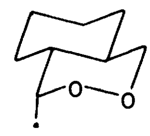
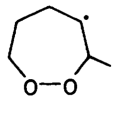
First let us consider the radicals derived from the acyclic β-bromoalkyl t-butyl peroxides. A comparison of rate constants for radicals (2) and (3) with that for β-t-butylperoxyethyl (1) reveals that progressive introduction of methyl groups at the carbon atom bearing the peroxy group (*i.e.* β to the radical centre) gives rise to a rate enhancement of approximately 20-fold for each methyl group. It has been noted previously [7] that this parallels the well known *gem*-dialkyl effect in heterolytic ring closures.[13] A comparison of radicals (2) and (6) now shows that a similar rate enhancement (*ca.* 25-fold) occurs when the second methyl group is introduced at the carbon atom bearing the unpaired electron. The thermodynamically more stable radicals are therefore more reactive. The simplest explanation that can be given for this rate enhancement is one in terms of polar effects in the transition state for ring closure.

The electronic structure of the transition state (Scheme 1) will involve a contribution by a canonical form with a carbocationic centre, which will be stabilised by alkylation. That the rate constants for the secondary radicals (4)—(8) are all higher than that for the primary radical (2) is consistent with this

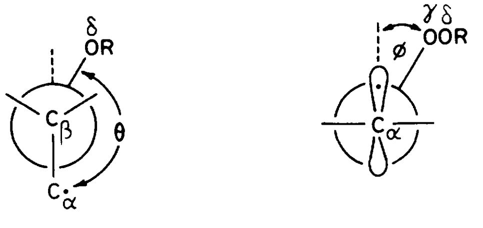


Scheme 1.

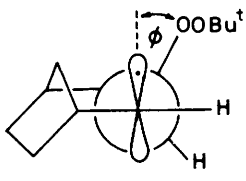
Table 2. Rate constant data at *ca.* 298 K for γ-scission in β-peroxyalkyl radicals derived from cyclic peroxides

	Radical	k_O/k_H mol dm^{-3}	k_O/s^{-1} [a]	k_O(rel) [b]
(9)		0.01 [c]	2×10^4	5
(10)		0.09 [c]	1.8×10^5	45
(11)		1.05 [c]	2.1×10^6	525
(12)		0.012 [d]	2.4×10^4	6
(13)		$<10^{-5}$ [d]	<20	$<5 \times 10^{-3}$
14)		$<10^{-6}$ [c]	<2	$<5 \times 10^{-4}$

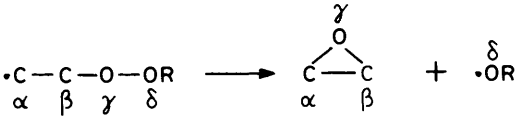
[a] Calculated by assuming $k_H = 2 \times 10^6$ dm^3 mol^{-1} s^{-1} (ref. 9). [b] k_O divided by rate constant for γ-scission in $CH_2(OOBu^t)\dot{C}H_2$ (Table 1). [c] Taken from ref. 11. [d] Deduced from ref. 12.



Scheme 2.



Scheme 3.



$$\cdot\underset{\alpha}{C}-\underset{\beta}{C}-\underset{\gamma}{O}-\underset{\delta}{O}R \longrightarrow \underset{\alpha}{C}\overset{\overset{\gamma}{O}}{—}\underset{\beta}{C} + \overset{\delta}{\cdot OR} \qquad (11)$$

polar effect being more important than the thermodynamic stability of the radicals. A similar argument has recently been advanced to account for the rate of addition of various alkyl radicals to vinylphosphonates.[14]

The reactivities which are observed for the radicals derived from cyclic β-bromoalkyl t-butyl peroxides, particularly the 3-*exo*-t-butylperoxytrinorbornan-2-yl radical (4), and Porter's cyclic peroxyalkyl radicals (9)—(14), require further consideration of the structure of the transition state shown in Scheme 1.

The transition state for the intramolecular homolytic substitution at oxygen [equation (11)] appears to require two conformational criteria to be fulfilled (Scheme 2). First, the torsion angle θ between the C_α–C_β bond and the O_γ–O_δ bond should be close to 180° to permit back-side approach of the radical ($C^\bullet_\alpha$) to the reaction centre (O_γ), with a linear disposition of C_α, O_γ, and O_δ in the transition state. Second, the torsion angle ϕ between the axis of the singly occupied *p*-orbital on C_α, and the C_β–O_γ bond, should be close to 0° to permit effective interaction between the *p*-orbital and the σ and σ* orbitals of the O_γ–O_δ bond which is to break.

The first (θ) criterion is ,predicted from theoretical considerations, and has been elegantly demonstrated by Porter's work with cyclic peroxides (Table 2).[11,12] Thus in the stereochemically rigid radicals (12) and (13), k_O for the equatorial isomer (12) is at least three orders of magnitude greater than k_O for the axial isomer (13). Again, in the isomeric radicals (11) and (14), the endocyclic species (14), which is constrained to attack the peroxide bond from the side, has a rate constant at least 10^6 times smaller than that for the exocyclic radical (11) where the favourable back-side approach is readily achieved.

A consideration of the primary radicals (2) and (12) and of the secondary radicals (6) and (11) suggests that rate constants for γ-scission are not very sensitive to the nature of the departing alkoxy group. That the rate constants for the dioxolanyl radicals (9) and (10) are, respectively, 70 and 34 times lower than those for the comparable t-butylperoxyalkyl radicals (3) and (8) can then be seen as a further manifestation of the steric barrier to internal homolytic substitution. It is more difficult for the five-membered ring to adopt conformations in which the Ċ–C–O–O torsion angle θ has the preferred value of 180°.

The 3-*exo*-t-butylperoxytrinorbornan-2-yl radical (4) can

Table 3. Data for reduction of β-bromoalkyl t-butyl peroxides

Confign. of bromo-peroxide	Initial concn. of bromo-peroxide (mol dm^{-3})	Initial concn. of Bu_3SnH (mol dm^{-3})	Molar ratio $\frac{\text{oxirane}}{\text{peroxide}}$	$\frac{k_O/k_H}{\text{mol dm}^{-3}}$ [a]
	2-Bromo-3-*exo*-t-butylperoxytrinorbornane			
trans	0.24	0.80	0.28	0.19
trans	0.240	1.364	0.088	0.11
cis	0.25	0.80	0.24	0.16
cis	0.247	1.371	0.14	0.18
			Average:	0.16
	1-Bromo-2-t-butylperoxycyclohexane			
trans	0.270	0.818	0.70	0.48
trans	0.252	1.371	0.39	0.48
trans	0.274	1.918	0.39	0.69
cis	0.251	0.784	0.70	0.52
cis	0.259	1.347	0.36	0.47
cis	0.251	1.918	0.37	0.68
			Average:	0.56
	2-Bromo-3-t-butylperoxybutane [b]			
threo	0.280	0.794	1.37	0.90
threo	0.276	1.375	0.75	0.93
threo	0.271	1.907	0.64	1.14
erythro	0.266	0.784	1.56	1.02
erythro	0.266	1.354	0.83	1.02
erythro	0.266	1.924	0.46	0.84
			Average:	0.98
	1-Bromo-2-t-butylperoxycyclopentane			
trans	0.326	0.798	0.95	0.60
trans	0.326	1.363	0.90	1.07
trans	0.340	1.901	0.83	1.43
trans	0.340	2.116	0.48	0.93
cis	0.326	0.781	1.05	0.65
cis	0.340	1.356	1.24	1.46
cis	0.340	1.897	0.57	0.97
cis	0.340	2.276	0.46	0.96
			Average:	1.0
	3-Bromo-4-t-butylperoxyhexane [c]			
threo	0.258	0.812	4.8	3.25
threo	0.312	1.370	2.7	3.28
threo	0.300	1.897	1.67	2.91
erythro	0.302	0.795	5.0	3.22
erythro	0.320	1.370	2.2	2.69
erythro	0.312	1.911	1.67	2.93
			Average:	3.1

[a] Calculated from the expression $\frac{k_O}{k_H} = \frac{[\text{oxirane}]}{[\text{peroxide}]} \times [Bu_3SnH]_{\frac{1}{2}}$, where $[Bu_3SnH]_{\frac{1}{2}}$ = concn. of Bu_3SnH at half reaction. [b] Yielded *trans*- and *cis*-oxirane in the average ratio of 3.6 : 1. [c] Yielded *trans*- and *cis*-oxirane in the average ratio of 7.7 : 1.

clearly meet the first of the two conformational criteria with $\theta = 180°$. If the radical were planar at C_α, the angle ϕ would be 30° (Scheme 3), and this might be thought to be the origin of its reduced reactivity. However, the e.s.r. spectra of a variety of trinorbornan-2-yl radicals show that a(*exo*-H-3) is greater than a(*endo*-H-3),[15] implying that the C(2)–H bond is distorted in the *endo*-direction, which would reduce the angle ϕ to near to zero. The radical (4) therefore appears to meet the conformational criteria for ring closure, and the reduced reactivity is probably to be associated with the extra angle strain induced in the oxirane ring when it is fused to the norbornyl skeleton.

Experimental

Materials.—The β-bromoalkyl t-butyl peroxides were prepared by peroxymercuriation and bromodemercuriation of non-terminal alkenes as described previously.[6b] Tributyltin hydride was prepared from bistributyltin oxide and polymethylhydrosiloxane,[16] and was redistilled under nitrogen (b.p. 80—81 °C at 0.3 mmHg) before use. Benzene (AnalaR grade) was dried over sodium and distilled under nitrogen.

Product Analyses.—The general procedure was as follows. Into a dry, nitrogen-flushed, graduated n.m.r. tube were placed, in the order given, (i) the β-bromoalkyl t-butyl peroxide (50—60 μl; exact quantity taken determined by weighing), (ii) tributyltin hydride (by graduated glass pipette, measured to nearest 50 μl; weight calculated using d_{20} = 1.103 g cm^{-3}), (iii) 1,3,5-trioxane (0.0986 mmol) in benzene (40 μl), (iv) hexadeuteriobenzene (100 μl), (v) tetramethylsilane (2 drops), (vi) benzene (to bring total volume to 1 cm^3), and (vii) di-t-butyl hyponitrite (20 μl of solution containing 183 mg in 1 cm^3 of benzene). The tube was shaken to mix the contents thoroughly and then was kept in a water bath at 20—25 °C before the 200 MHz ^{1}H n.m.r. spectrum was recorded using a Varian XL 200 spectrometer.

Product analyses were carried out using spectra recorded when the reactions had gone to completion, namely 2—6 h after mixing, except for the 2-bromo-3-*exo*-t-butylperoxytrinorbornanes in which case times of 1—2 d were required. Signals corresponding to the protons attached to the carbon atoms of the oxirane ring and to the carbon atom bearing the t-butylperoxy group (identified from published data[17]) were expanded and areas were measured by electronic integration and checked by square counting on graph paper tracings of the original spectra. The molar ratios of oxirane to peroxide were calculated from these areas and the individual results, along with the rest of the data for each experiment, are shown in Table 3.

For each reaction, the product accountability, *i.e.* the yield of oxirane plus peroxide as a molar fraction of the β-bromoalkyl t-butyl peroxide taken, was calculated by comparing the product integrals with that for the added trioxane. The $Bu_3Sn\mathit{H}$ signal showed a slightly variable chemical shift and sometimes caused difficulty in recording reliable integrals for the trioxane. In these instances the product accountability could not be satisfactorily assessed, but where the problem did not arise, the product accountability was consistently high (>85%).

Acknowledgements

We thank the S.E.R.C. for a research studentship (to J. L. C.), and Dr. B. P. Roberts for discussion.

References

1 (*a*) J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, 1948, **70**, 2767; (*b*) E. R. Bell, F. F. Rust, and W. E. Vaughan, *ibid.*, 1950, **72**, 337.
2 L. Batt and S. W. Benson, *J. Chem. Phys.*, 1962, **36**, 895.
3 (*a*) F. R. Mayo, *J. Am. Chem. Soc.*, 1958, **80**, 2465; (*b*) F. R. Mayo and A. A. Miller, *ibid.*, p. 2480; (*c*) p. 2493; (*d*) F. R. Mayo, *ibid.*, p. 2497; (*e*) F. R. Mayo, A. A. Miller, and G. A. Russell, *ibid.*, p. 2500.
4 A. P. Zeelenberg and A. F. Bichel, *J. Chem. Soc.*, 1961, 4014.
5 A. Fish in ' Oxidation of Organic Compounds,' vol. II, ed. F. R. Mayo, A.C.S. Advances in Chemistry Series, 1968, No. 76, p. 69.
6 (*a*) A. J. Bloodworth and I. M. Griffin, *J. Chem. Soc., Perkin Trans. 1*, 1975, 695; (*b*) A. J. Bloodworth and J. L. Courtneidge, *ibid.*, 1981, 3258.

7 (*a*) A. J. Bloodworth, A. G. Davies, I. M. Griffin, B. Muggleton, and B. P. Roberts, *J. Am. Chem. Soc.*, 1974, **96**, 7599; (*b*) B. Muggleton, Thesis, London, 1975.
8 D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, 1968, **90**, 7047.
9 C. Chatgilialoglu, K. U. Ingold, and J. C. Scaiano, *J. Am. Chem. Soc.*, 1981, **103**, 7739.
10 (*a*) H. G. Kuivila, *Acc. Chem. Res.*, 1968, **1**, 299. (*b*) A. G. Davies in ‘Organotin Compounds: New Chemistry and Applications,’ ed. J. J. Zuckerman, A.C.S. Advances in Chemistry Series, 1976, No. 157, p. 26.
11 N. A. Porter and J. R. Nixon, *J. Am. Chem. Soc.*, 1978, **100**, 7116.
12 N. A. Porter, M. A. Cudd, R. W. Miller, and A. T. McPhail, *J. Am. Chem. Soc.*, 1980, **102**, 414.
13 C. J. M. Stirling, *Isr. J. Chem.*, 1981, **21**, 111.
14 J. E. Baban and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1981, 161.
15 J. Gloux, M. Guglielmi, and H. Lemaire, *Mol. Phys.*, 1970, **19**, 833; R. Marx and L. Bonazzola, *ibid.*, p. 899; T. Kawamura, T. Toyama, and T. Yonezawa, *J. Am. Chem. Soc.*, 1973, **95**, 3220.
16 K. Hayashi, J. Iyoda, and I. Shiihari, *J. Organomet. Chem.*, 1967, **10**, 81.
17 A. J. Bloodworth and J. L. Courtneidge, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1797.

Received 28*th July* 1983; *Paper* 3/1268