The Reaction of t-Butoxyl Radicals with Diborane

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The reaction of butoxyl radicals with diborane has been shown by e.s.r. spectroscopy to yield t-butyl radicals. The rate constant for this process is given by $k = 10^{8\cdot4} \times 10^{2\cdot9/\theta}$ l mol^{-1} s^{-1} where $\theta = 2\cdot303\,RT$ in kcal mol^{-1}. No intermediate 4-co-ordinate boron radical could be detected. Analogies are drawn with t-butoxyl–trialkyl phosphite reaction and with the oxidation of trialkylboranes by alkaline hydrogen peroxide and by amine oxides. t-Butyl radicals are not formed in detectable quantities in either the t-butoxyl–alkyldiborane or in the t-butoxyl–phosphine reactions.

THE unequivocal identification by e.s.r. spectroscopy of the intermediates, $\mathrm{ZY\dot{M}X}_n$, involved in the homolytic reactions of radicals ZY· at multivalent atoms, M, has been confined so far to reactions involving the Group V elements phosphorus [1-5] and arsenic [6,7] in their tervalent

$$\mathrm{ZY\cdot} + \mathrm{MX_3} \rightarrow \mathrm{ZY\dot{M}X_3} \begin{cases} \xrightarrow{\alpha} \mathrm{ZYMX_2} + \mathrm{X\cdot} & \text{(1a)} \\ \xrightarrow{\beta} \mathrm{Z\cdot} + \mathrm{Y{=}MX_3} & \text{(1b)} \end{cases}$$

states. Analogous four-co-ordinate species have not been detected in reactions involving Group III elements despite numerous attempts, particularly with compounds of boron [2,8-14] and aluminum.[2,8,10] The failure to detect such intermediates may in part be due to the extreme rapidity of many bimolecular homolytic substitutions [reactions (1a)] at Group III elements.[9-17]

In the case of phosphorus, it has recently been shown that steric crowding around the central atom probably has an important bearing on the stability of phosphoranyl —70 °C yield initially the corresponding phosphoranyl radicals, $\mathrm{Bu^tO\dot{P}X_3}$, while with $\mathrm{Me_3P}$ both the phosphoranyl and methyl radicals are formed, and with $\mathrm{Et_3P}$ only the ethyl radical is formed. Similarly, it has been found that the stabilities towards β-scission [reaction (1b)] of $\mathrm{Bu^tO\dot{P}(OR)_3}$ radicals decrease by about an order of magnitude along the series R = Me, Et, Pr^i, radicals.[5] Thus [5] the reactions of t-butoxyl radicals with $\mathrm{PH_3}$, $\mathrm{MePH_2}$, and $\mathrm{Me_2PH}$ at temperatures below Bu^t.[18] Steric crowding is likely to have an even greater effect with boron because of its smaller size. For this reason we have examined the reaction of t-butoxyl radicals with diborane by e.s.r. spectroscopy in the hope of observing the four-co-ordinate boron radical, $\mathrm{Bu^tO\dot{B}H_3}$. Some experiments with partially alkylated diboranes and with phosphine have also been carried out.

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[4] A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 993.

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[6] A. G. Davies, D. Griller, and B. P. Roberts, *J. Organometallic Chem.*, 1972, **38**, c8.

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[9] A. G. Davies and B. P. Roberts, *Chem. Comm.*, 1969, 699.

[10] A. G. Davies and B. P. Roberts, *J. Organometallic Chem.*, 1969, **19**, 817.

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RESULTS

Diborane.—Photolysis in the e.s.r. cavity of deoxygenated solutions of di-t-butyl peroxide and diborane in cyclopropane at molar ratios of 1 : 1·5 : 7·5 yielded a moderately intense spectrum of the t-butyl radical over a temperature range from +25 to *ca.* −90 °C. At temperatures in the range −100 to −120 °C the intensity of the t-butyl signal decreased. At no temperature could any other e.s.r. signal be detected. In particular, there was no signal that could be attributed to $Bu^tO\dot{B}H_3$, nor to a radical resulting from hydrogen abstraction from the diborane ($H_2B\cdot$ or $H_5B_2\cdot$), nor was the characteristic doublet due to hydrogen atoms present [*i.e.*, there is no e.s.r. evidence for reaction (1a)]. Hydrogen gas was formed in the reaction which implies that the oxygenated borane is unstable, *e.g.*, reaction (3).

$$Bu^tO\cdot + B_2H_6 \longrightarrow Bu^{t}\cdot + [HOBH_2BH_3 \text{ or } HOBH_2 + BH_3] \qquad (2)$$

$$[HOBH_2BH_3] \longrightarrow H_2BOBH_2 + H_2 \qquad (3)$$

At room temperature a mixture of equal liquid volumes of di-t-butyl peroxide and diborane without any co-solvent did not undergo any observable reaction in 24 h in the absence of light. By contrast, when diborane was distilled at liquid-nitrogen temperatures on to a dilute solution of diethyl peroxide in cyclopentane, the e.s.r. tube exploded within seconds of the liquid nitrogen being removed. The equi-volume di-t-butyl peroxide–diborane mixture was homogeneous at temperatures down almost to the f.p. of the peroxide (*ca.* −40 °C).* Photolysis at −38 °C yielded only the t-butyl radical which was present in smaller amounts than in the more dilute reaction mixtures. After 3 or 4 days at room temperature the material in this e.s.r. tube solidified.

In order to determine the rate of reaction (2) experiments were carried out in cyclopentane as solvent and the relative concentrations of t-butyl and cyclopentyl radicals were measured.

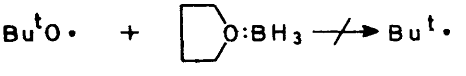
$$Bu^tO\cdot + C_5H_{10} \longrightarrow Bu^tOH + C_5H_9\cdot \qquad (4)$$

This technique has been used with considerable success in a number of related studies.[3,4,12,19] At low diborane concentrations (0·5—1·0 mole % of the cyclopentane) the $[Bu^{t}\cdot] : [C_5H_9\cdot]$ ratio was directly proportional to the $[B_2H_6] : [C_5H_{10}]$ ratio and the concentrations of both radicals were proportional to the square root of the light intensity.† Because of the low diborane concentration the t-butyl radical persisted for only 5—10 min. It was therefore necessary to extrapolate the t-butyl radical concentrations measured during this interval back to time zero (the start of irradiation) in order to obtain the true relative reactivity of diborane and cyclopentane.‡ The results are summarized in the Table.

Reaction of $Bu^tO\cdot$ with diborane in equimolar di-t-butyl peroxide–cyclopentane mixtures

t/°C	$\frac{100[B_2H_6]}{[C_5H_{10}]}$	$\frac{100[Bu^{t}\cdot]}{[C_5H_9\cdot]}$	$\frac{[Bu^{t}\cdot][C_5H_{10}]}{[C_5H_9\cdot][B_2H_6]}$
0	0·83	$10\cdot_5$	$12\cdot_5$
−8	0·50	10	20
−29	0·58	16	$27\cdot_5$
−39	1·0	$28\cdot_5$	$28\cdot_5$
−49	0·50	$18\cdot_5$	37

Diborane–Tetrahydrofuran.—t-Butyl radicals were not produced by the photolysis of a mixture of peroxide, tetrahydrofuran, and diborane in a molar ratio 2 : 2 : 1 at 20 or at −40 °C, nor could any other radical be detected.

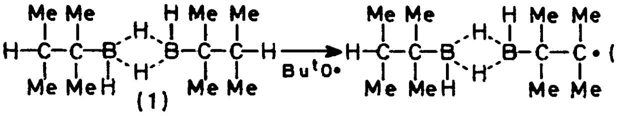


(5)

Presumably the t-butyl radical is not formed because the tetrahydrofuran is too strongly co-ordinated with BH_3 for it to be displaced by t-butoxyl radical.

The photolysis of peroxide–tetrahydrofuran mixtures yields a strong e.s.r. signal due to the tetrahydrofuran-2-yl radical. The absence of an analogous species from the tetrahydrofuran–borane complex may be due to the strengthening of the α-C–H bonds by the electron-withdrawing BH_3 group. Some reaction must however occur on photolysis since hydrogen gas is produced.

Partially Alkylated Diboranes.—Photolysis of di-t-butyl peroxide containing *sym*-bis-(1,1,2-trimethylpropyl)diborane[20–22] (1) gave a rather weak and poorly resolved e.s.r. signal containing a number of lines, the number depending on the temperature. At low temperatures (−30 to −100 °C in cyclopropane) there were about 13 rather unevenly spaced, broad (ΔH ≳ 3 G), asymmetric lines, the main lines being separated by *ca.* 22 G. At higher temperatures (0—100 °C) a somewhat larger number of much narrower lines were obtained. The spectrum does not correspond to that of the $Bu^{t}\cdot$, $Me_2CH\dot{C}Me_2$, or $Me_2C{=}CMe\dot{C}H_2$ radicals, though it is possible that one or more of these radicals is present in small amounts. The majority § of the high temperature lines can be analysed in terms of a doublet (a_H = *ca.* 12 G) of heptets (a_H = *ca.* 22 G). This is not inconsistent with a radical produced by abstraction of a tertiary hydrogen atom from (1) if it is assumed that the heptet due to the two adjacent methyl groups is split by the free hydrogen on the closest boron atom (which is probably in fairly close proximity to the orbital occupied by the unpaired electron).



(6)

Tetracyclohexyldiborane[20,21] (2) is extremely insoluble in organic solvents. Photolysis of saturated solutions in

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* Diborane is quite soluble in hydrocarbons. See *e.g.*, L. V. McCarty and J. Guyon, *J. Phys. Chem.*, 1954, **58**, 285.

† At higher $[B_2H_6] : [C_5H_{10}]$ ratios the order in light intensity was between 0·5 and 1·0 and, moreover the $[Bu^{t}\cdot] : [C_5H_9\cdot]$ ratio was no longer linearly related to the $[B_2H_6] : [C_5H_{10}]$ ratio. Apparently alkyl radicals can react directly with diborane. This was confirmed by an experiment in which t-butyl radicals were generated at −30 °C by the photolysis of a di-t-butyl peroxide–isobutane mixture (mole ratio 1 : 1). The addition of diborane (0·5 mol) *reduced* the steady-state t-butyl concentration by *ca.* 35%.

‡ Although the t-butyl signal is much less intense at the higher temperatures, it does not persist for any longer than at low temperatures, presumably because the diborane is consumed by reaction with the t-butyl alcohol formed in reaction (4).

§ Some four or six lines remain unaccounted for but they could be due to the presence of a small amount of t-butyl radicals.

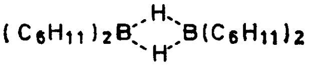
[19] D. Griller and B. P. Roberts, *Chem. Comm.*, 1971, 1035.

[20] H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, 1962, **84**, 1478.

[21] H. C. Brown and G. J. Klender, *Inorg. Chem.*, 1962, **1**, 204.

[22] G. Zweifel and H. C. Brown, *J. Amer. Chem. Soc.*, 1963, **85**, 2066.

di-t-butyl peroxide yielded e.s.r. spectra that were too weak to analyse.



(2)

Diborane–Disulphide and Diborane–Tetrazene. The possibility that thiyl or aminyl radicals would react with diborane in a manner analogous to t-butoxyl was briefly examined. Photolysis of neat di-t-butyl disulphide gives mainly t-butylthiyl radicals but some t-butyl radicals are also formed and can be detected by e.s.r. spectroscopy.[11] The addition of diborane to this disulphide suppressed the t-butyl e.s.r. signal and no other radical could be detected. Addition of diborane to dimethyl disulphide resulted in rapid hydrogen evolution at room temperature and so photolysis was not attempted. Diborane and tetramethyltetrazene exploded immediately following the removal of the liquid nitrogen used to condense the diborane on the tetrazene.

Phosphine.—Krusic *et al.*[5] have found that photochemically generated t-butoxyl radicals react with phosphine at temperatures below −70 °C to yield two different phosphoranyl radicals, $P_1\cdot$ and $P_2\cdot$. The radical $P_1\cdot$ is formed immediately upon irradiation and is almost certainly $Bu^tO\dot{P}H_3$ [a_P = 626·7 G, a_H 139·6 G (doublet), and a_H = 10·8 G (triplet)]. The radical $P_2\cdot$ must be formed from some product of photolysis since it takes a few minutes to develop. The spectrum of two lines (a_P = 672·5 G) each of which had unresolved shoulders possibly indicating a small (a = 0·6 G) triplet splitting. It was suggested that the second radical is $(Bu^tO)_2\dot{P}H_2$. Steady-state conditions are achieved in a few minutes and under such conditions $P_1\cdot$ predominates at temperatures below −100 °C and $P_2\cdot$ above −100 °C.

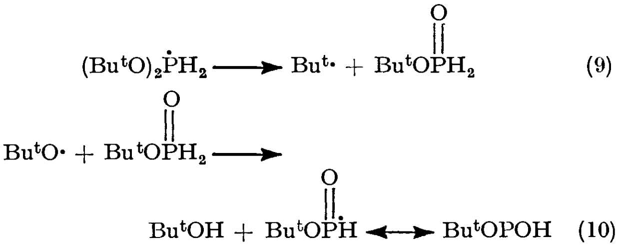
We have confirmed the above observations in experiments that were started with the object of comparing the stability of $Bu^tO\dot{P}H_3$ towards β-scission (decomposition to $Bu^t\cdot$ and H_3PO) with the stability of our hypothetical $Bu^tO\dot{B}H_3$ species. At −100 °C in cyclopropane both $P_1\cdot$ and $P_2\cdot$ decay within the time constant of the spectrometer. Under steady-state conditions the concentrations of $P_1\cdot$ and of $P_2\cdot$ are proportional to the square root of the light intensity indicating that both radicals disappear solely by reactions with other radicals. No other radical appears even on prolonged photolysis at −100 °C. On raising the temperature a new phosphorus-containing radical, $P_3\cdot$, appears (see below) but t-butyl radicals cannot be detected even at +30 °C. This does not necessarily mean that neither $P_1\cdot$ nor $P_2\cdot$ decomposes unimolecularly to form t-butyl radicals at this temperature since $Bu^t\cdot$ appears to be rapidly destroyed by phosphine.* In fact, the steady-state concentrations of $P_1\cdot$ and $P_2\cdot$ are both approximately proportional to (light intensity) $^{0\cdot8}$ at 30 and at 0 °C which indicates that they are in part destroyed by unimolecular processes at such temperatures, though they decay entirely bimolecularly at −50 °C.

The new radical $P_3\cdot$ shows only a doublet [$a(^{31}P)$ = 83·3 G, g = 2·003, in di-t-butyl peroxide at room temperature †] which cannot be further resolved (line-width *ca.* 0·8 G). It is formed on photolysis of the peroxide–phosphine mixture at 0 °C and above. Once the sample has been photolysed at such temperatures then $P_3\cdot$ can be seen (on irradiation) even at temperatures as low as −100 °C though its intensity is much reduced compared with high temperatures. Apparently $P_3\cdot$ is formed from a photolysis product that is itself formed only at higher temperatures. This is indicated by the fact that at +30 °C in a fresh (unphotolysed) peroxide–phosphine mixture $P_3\cdot$ does not start to form for 10—15 s after the start of irradiation whereas $P_2\cdot$ (which is formed slowly at low temperatures) is formed immediately, perhaps *via* the sequence (7) and (8). At all temperatures $P_3\cdot$ decays within the time constant of the spectrometer. Its steady-state concentration is proportional to (light intensity) $^{0\cdot3-0\cdot4}$ in the temperature range −50 to +30 °C. The low value of this exponent could arise if $P_3\cdot$ is formed by unimolecular decomposition of $P_2\cdot$ (or $P_1\cdot$) and is destroyed both by a bimolecular self-reaction and by reaction with $P_2\cdot$.

$$Bu^tO\cdot + PH_3 \longrightarrow Bu^tOH + \dot{P}H_2 \qquad (7)$$

$$\cdot PH_2 + Bu^tOOBu^t \longrightarrow (Bu^tO)_2\dot{P}H_2 \qquad (8)$$

The magnitude of the coupling constant for $P_3\cdot$ suggests that it is a phosphinyl radical. Thus, for example, for $\cdot PF_2$ $a(^{31}P)$ = 84·6 G,[23] for $\cdot PCl_2$ $a(^{31}P)$ = 71 G,[24] and for $\cdot PH_2$ $a(^{31}P)$ = 80 G.[25] The $\cdot PH_2$ radical is the obvious candidate for $P_3\cdot$ but this seems unlikely as $PH_2\cdot$ is reported[25] to show splittings from the two equivalent hydrogens (a_H = 18 G), while $P_3\cdot$ shows only a simple doublet. Potential candidates for $P_3\cdot$ are $(HO)_2P\cdot$, $Bu^tO\dot{P}OH$, and $(Bu^tO)_2P\cdot$, *e.g.* reactions (9) and (10).



$$(Bu^tO)_2\dot{P}H_2 \longrightarrow Bu^t\cdot + Bu^tOP(=O)H_2 \qquad (9)$$

$$Bu^tO\cdot + Bu^tOP(=O)H_2 \longrightarrow Bu^tOH + Bu^tO\dot{P}(=O)H \longleftrightarrow Bu^tO\dot{P}OH \qquad (10)$$

Attempts to generate the $P_3\cdot$ spectrum by photolysing di-t-butyl peroxide with hypophosphorous acid, $H_2P(O)OH$, with tetrahydrofuran or t-butyl alcohol as cosolvents did not yield $P_3\cdot$, nor was any other radical detected. However, photolysis of a solution of tetraethoxydiphosphine in di-t-butyl peroxide at room temperature gave a simple doublet, $a(^{31}P)$ = 78·5 G, g 2·002, line-width 0·6 G. This radical is probably $(EtO)_2P\cdot$. Its spectral parameters provide some support for the view that $P_3\cdot$ is a dialkoxy-(or hydroxy)-phosphinyl radical. The work on this and other phosphinyl radicals will be reported later.

The complex nature of the reactions occurring in the peroxide–phosphine system ruled out any attempt to study these processes kinetically.

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* t-Butyl radicals were generated by photolysis of azoisobutane in cyclopentane at −50 °C. The e.s.r. signal due to these radicals was destroyed by the addition of PH_3.

† E.s.r. parameters were determined using the measured line positions and the microwave frequency in conjunction with the Breit–Rabi formula (P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967, p. 238).

[23] W. Nelson, G. Jackel, and W. Gordy, *J. Chem. Phys.*, 1970, **52**, 4572; *cf.* also D. Kilcast and C. Thomson, *J.C.S. Faraday II*, 1972, **68**, 435.

[24] G. F. Kokoszka and F. E. Brinckmann, *Chem. Comm.*, 1968, 349; *J. Amer. Chem. Soc.*, 1970, **92**, 1199.

[25] R. L. Morehouse, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, 1966, **45**, 1747.

DISCUSSION

t-Butoxyl radicals undergo rapid bimolecular homolytic substitutions with trialkylboranes and yield the appropriate alkyl radical in amounts that can be detected by e.s.r. spectroscopy.[2,8,10,12] Analogous reactions apparently do not occur with diborane, nor with the tetrahydrofuran–borane complex nor with alkyldiboranes.

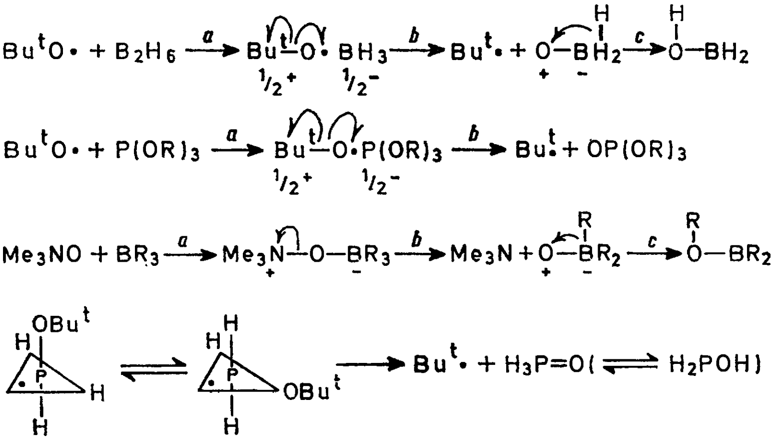
$$Bu^tO\cdot + BR_3 \longrightarrow Bu^tOBR_2 + R\cdot \qquad (11)$$

The reactivity of 3-co-ordinate boron towards attack by t-butoxyl is greater than that of the 4-co-ordinate boron in the tetrahydrofuran–borane complex and in the *sym*-alkyldiboranes * owing to the presence of the vacant *p* orbital. The occurrence of a diborane–t-butoxyl reaction may be due to t-butoxyl substituting for BH_3. (The heat of dimerization of BH_3 is $36 + 3$ kcal mol^{-1} of B_2H_6 formed.[27])

$$Bu^tO\cdot + B_2H_6 \longrightarrow Bu^tO\dot{B}H_3 + BH_3 \qquad (12)$$

The diborane–t-butoxyl reaction appears to be a variant of the β-scission process which frequently occurs when an alkoxyl radical reacts at a metal centre. For clarity, the various bond-forming and bond breaking processes are represented as separate steps in equation (13). Steps *a* and *b* are similar to those involved in, for example, the t-butoxyl–trialkyl phosphite reaction and subsequent β-scission. The nucleophilic 1,2-rearrangement of the hydrogen from boron to oxygen in step (13*c*) is similar to that which occurs in the oxidation of a trialkylborane with alkaline hydrogen peroxide [28] and with amine oxides,[29] *e.g.*, (15). By analogy with the hydrogen peroxide and amine oxide reactions it is probable that the homolysis (13*b*) occurs synchronously with the intramolecular nucleophilic rearrangement (13*c*).

The low stability of $Bu^tO\dot{B}H_3$ which, since it is not detectable by e.s.r. spectroscopy, may be merely a transition state in reaction (13), contrasts with the much greater stability of $Bu^tO\dot{P}H_3$ which is detectable at temperatures up to 30 °C.† The elimination of a t-butyl radical from both species will be highly exothermic and the differences in stability may reflect differences in the modes of decomposition of the two species. The borane adduct, with seven bonding electrons, is presumably tetrahedral while the phosphine adduct with nine bonding electrons is believed to be a slightly distorted trigonal bipyramid with the Bu^tO group in an apical and the unpaired electron in an equatorial position.[5] The dependence of the steady-state concentration of $Bu^tO\dot{P}H_3$ on light intensity indicates a bimolecular decay process at temperatures below -50 °C. At higher temperatures there is probably some unimolecular decomposition of $Bu^tO\dot{P}H_3$ to $H_3P{=}O$ and a t-butyl radical. The unimolecular decay probably requires a pseudorotation to bring the t-butoxy-group into the equatorial plane [18,30] and even then decomposition probably requires a significant activation energy.[18]



$$Bu^tO\cdot + B_2H_6 \xrightarrow{a} \overset{1/2+}{Bu^t}{-}\overset{1/2-}{O\cdot}\,BH_3 \xrightarrow{b} Bu^t\cdot + \overset{+}{O}{-}\overset{-}{B}H_2(H) \xrightarrow{c} HO{-}BH_2 \qquad (13)$$

$$Bu^tO\cdot + P(OR)_3 \xrightarrow{a} \overset{1/2+}{Bu^t}{-}\overset{1/2-}{O\cdot P(OR)_3} \xrightarrow{b} Bu^t\cdot + OP(OR)_3 \qquad (14)$$

$$Me_3NO + BR_3 \xrightarrow{a} Me_3\overset{+}{N}{-}O{-}\overset{-}{B}R_3 \xrightarrow{b} Me_3N + \overset{+}{O}{-}\overset{-}{B}R_2(R) \xrightarrow{c} RO{-}BR_2 \qquad (15)$$

$$\longrightarrow Bu^t\cdot + H_3P{=}O\,(\rightleftharpoons H_2POH) \qquad (16)$$

Since the t-butyl and cyclopentyl radical concentrations were proportional to the square root of the light intensity under the competitive conditions used (Table) these two radicals must be destroyed only in radical–radical reactions. Provided the rate constants for the bimolecular self-reactions of t-butyl ($2Bu^t\cdot \longrightarrow$ products) and cyclopentyl ($2C_5H_9\cdot \longrightarrow$ products) radicals are approximately the same, as is probably the case,[31] the relation (17) obtains.

$$k_2/k_4 = [Bu^t\cdot][C_5H_{10}]/[C_5H_9\cdot][B_2H_6] \qquad (17)$$

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* Even in tetrahydrofuran these compounds are diboranes which indicates how strongly the bridging hydrogens hold the two halves of these molecules together. By contrast, it is noteworthy that substitution does occur with di-isobutylaluminium [8] which is largely trimeric in solution: [26] $Bu^tO\cdot + (Bu^i_2AlH)_3 \longrightarrow Bu^i\cdot$.

† At temperatures above -60 °C the four outermost lines of the doublet of triplet spectra broaden and only the two sharp inner lines can be detected above $-30°$ (P. J. Krusic and P. Meakin, personal communication).

[26] E. G. Hoffmann, *Annalen*, 1960, **629**, 104.

[27] T. P. Fehlner and G. W. Mappes, *J. Phys. Chem.*, 1969, **73**, 873.

[28] A. G. Davies, *Progr. Boron Chem.*, 1964, **1**, 280.

[29] A. G. Davies and B. P. Roberts, *J. Chem. Soc.* (*C*), 1968, 1474.

[30] A. G. Davies, R. W. Dennis, D. Griller, and B. P. Roberts, *J. Organometallic Chem.*, 1972, **40**, c33.

[31] See, *e.g.*, D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, 1968, **90**, 7647; G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 491; K. U. Ingold, in ' Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973.

The data in the Table can be represented by equation (18) where $\theta = 2\cdot303RT$ in kcal mol^{-1}. The estimated[12]

$$k_2/k_4 = 10^{-0\cdot6} \times 10^{2\cdot3/\theta} \qquad (18)$$

dependence of k_4 on temperature is given by equation (19) and hence equation (20) follows. The pre-exponential factor is in the usual range for a fairly simple

$$k_4 = 10^{9\cdot0} \times 10^{-5\cdot2/\theta}\ \mathrm{l\ mol^{-1}\ s^{-1}} \qquad (19)$$

$$k_2 = 10^{8.4} \times 10^{-2.9/\theta}\ \mathrm{l\ mol^{-1}\ s^{-1}} \qquad (20)$$

radical–molecule reaction. The low activation energy (2·9 kcal mol^{-1}) is consistent with a highly exothermic process.* Diborane can be added to the growing list of reagents which includes phosphites[1-5,18,26] and carbon monoxide[19,32] that are known to deoxygenate the t-butoxyl radical. Our failure to detect $Bu^tO\dot{B}H_3$ is disappointing since the appropriate intermediate radicals have been identified with the above-mentioned reagents.

EXPERIMENTAL

The general experimental procedure has been outlined.[12] Reagents were handled and metered into e.s.r. tubes on a high-vacuum line.

Diborane was prepared from sodium borohydride and mercurous chloride.[33] *sym*-bis-(1,1,2-trimethylpropyl)diborane and *sym*-tetracyclohexyldiborane were prepared by reaction of the appropriate quantities of diborane and olefin in tetrahydrofuran for 1 h at 0 °C.[20-22] The tetrahydrofuran was then removed under vacuum and was replaced by di-t-butyl peroxide. Inversion of the reaction vessel allowed the solution to flow directly into the e.s.r. tube.

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* Compare $k = 10^{9\cdot8} \times 10^{-2\cdot24/\theta}$ l mol^{-1} s^{-1} for the reaction[3] $Bu^tO\cdot + (EtO)_3P \longrightarrow Bu^t\cdot + (EtO)_3PO$.

[32] E. A. Lissi, J. C. Scaiano, and A. E. Villa, *Chem. Comm.*, 1971, 457.

[33] G. E. Freeguard and L. H. Long, *Chem. and Ind.*, 1965, 471.