

Autoxidation of organoboranes and related organometallics: radicals and their ramifications

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The identification, 50 years ago, of the autoxidation products of organoboranes as organoperoxyboranes, and of the mechanism of the reaction as a radical chain, has had far-reaching consequences in organometallic and organic chemistry in the identification of organic radicals and of other radical reactions, in the use of organoboron compounds in synthesis and catalysis, in the parallel chemistry of other metals (particularly, currently, of zinc), and of the behaviour of metals as hydrogen equivalents. This review traces the course of some of those developments in the radical chemistry of compounds in which oxygen forms a bond with boron and related metals, and summarises the present position.

Keywords: autoxidation, peroxides, hydroperoxides, radicals, organoboranes, organozinc

1 Introduction

In 1859, Frankland prepared triethylborane, Et₃B, from triethyl borate and diethylzinc, and reported that “the liquid is spontaneously inflammable in air, burning with a beautiful green and somewhat fuliginous flame ... the temperature of which is so low that a finger may be held in it for some time without much inconvenience. In contact with pure oxygen, it explodes.”^{1,2} When it was allowed to oxidise gradually, it gave EtB(OEt)₂. Trimethylborane, which is a gas, behaved similarly,¹ and this reaction provides a spectacular lecture demonstration. The pyridine adduct of trimethylborane is a stable, crystalline solid. If it is dissolved in a little alcohol, and an acid is added, trimethylborane is evolved, and when it meets the air it ignites with a green flame, giving smoke rings of white boron oxide.

Little interest was shown in this spontaneous oxidation for the next century, until the burgeoning of organometallic chemistry in the 1950s, when it was shown that the initial products are organoperoxyboranes, and then that the oxidation follows a radical chain mechanism. The recognition of this has had remarkably wide ramifications in the identification of organic radicals and of other radical reactions, in the use of organoboron compounds in synthesis and catalysis, in the parallel chemistry of other metals (particularly, currently, of zinc), and of the behaviour of metals as hydrogen equivalents.

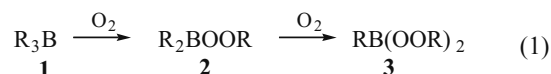
This chemistry is the concern of the present article, which focuses on organoboron compounds and oxygen-centred radicals, together with the parallel, less extensive, chemistry of the organic compounds of other metals, particularly zinc. There are some excellent reviews of some aspects of the field, (organoboranes as a source of radicals,³ organoborane initiators of radical chain reactions,⁴ tin-free radical reactions mediated by organoboron compounds,⁵ and B-alkylcatecholborane-mediated radical reactions⁶) but we have been involved in this chemistry since the 1950 s, and a personal perspective might be useful. I have tried to avoid, as much as possible, overlap with these existing reviews, but rather to give a picture of the many remarkable, and continuing, developments in organometallic, synthetic organic, and physical organic chemistry which this

simple reaction can be regarded as having spawned. Reactions involving other heteroatomic-centred radicals, though extensive, are not included.

2 The formation of alkylperoxyboranes

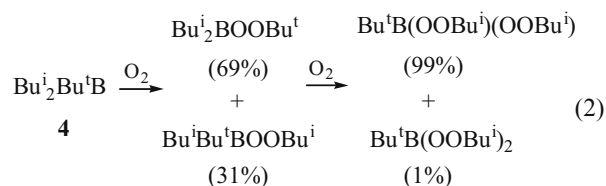
There were plenty of hints in the literature that the autoxidation of organoboranes should give peroxides: The products had been shown to oxidise iodide to iodine, and in 1965, Walling showed that alkyl hydroperoxides could be isolated from the autoxidation of Grignard reagents.⁷

In 1957, it was shown that, when trialkylboranes (**1**) in dilute solution are exposed to dioxygen, the primary products are the monoperoxyboranes (**2**) or the diperoxyboranes (**3**), which can be isolated as oils which are fairly stable at room temperature, but are readily hydrolysed in air.



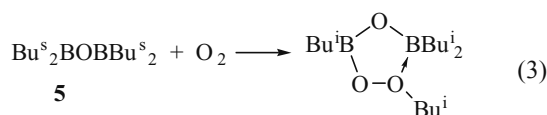
Trimethylborane (**1**, R = Me), in the gas phase, gives the monoperoxide (**2**)⁸ but most higher alkylboranes, **1**, R = Bu,⁹⁻¹² s-Bu,^{12,13} Buⁱ,^{14,15} and BuMeCH¹⁶ give the diperoxyboranes (**3**). This marked difference in the behaviour of the methyl derivative and the higher homologues is common in organometallic chemistry (and crops up again in this review). Aryl- and vinyl-boranes show more complicated behaviour because of the intrinsic instability of the aryl and vinyl peroxides.

The reactions are exothermic and the first molar equivalent of dioxygen usually reacts twice as fast as the second. With diisobutyl-t-butylborane, **4**, the t-butyl group is more mobile than the iso-butyl group, giving in sequence, the monoperoxyboranes and the diperoxyboranes in the proportions shown in equation (2).¹⁷

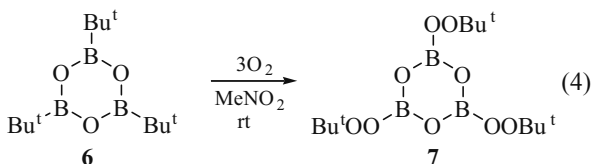


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s-Butylborinic anhydride, **5**, gives the monoperoxide, probably intramolecularly associated (equation (3)).¹³



Methylboronic anhydride (trimethylboroxine) is unreactive, but the butylboronic anhydrides show a reactivity of the alkyl group R in the sequence $\text{Bu}^s \cong \text{Bu}^t > \text{Bu}^n$, the t-butyl compound, **6**, in nitromethane absorbing 3 mol. of dioxygen to give a 93% yield of the triperoxide **7**.¹⁸

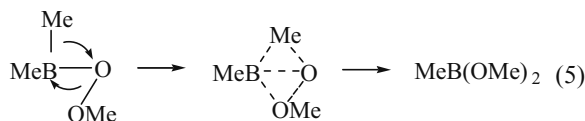


In general, the reactivity of organoboron compounds towards oxygen follows the sequences:

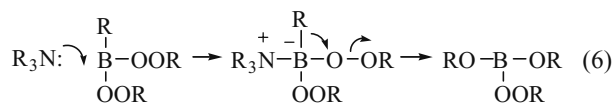
$\text{R}_3\text{B} > \text{R}_2\text{BX} > \text{RBX}_2$ (X = halogen, OR, OOR, or OH);
 $\text{R}_2\text{BF} > \text{R}_2\text{BCl} > \text{R}_2\text{BBr} > \text{R}_2\text{BI}$; $\text{R}_2\text{BOH} > \text{R}_2\text{BOR} > \text{R}_2\text{BONa}$;
 AlkylB > ArylB \cong VinylB; $\text{R}^t\text{B} > \text{R}^s\text{B} > \text{R}^n\text{B} > \text{MeB}$.

It is enhanced by the electropositive nature of the metal centre and by the presence of a low-lying vacant orbital, and may be hindered by steric congestion about the boron centre. More examples of the autoxidation are given below.

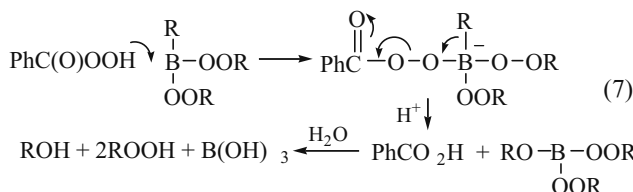
Dimethyl(methylperoxyborane) forms a crystalline adduct with ammonia or pyridine. The peroxide slowly decomposes to methyl(dimethoxy)borane. In the gas phase, the reaction shows first order kinetics, with a half life of 60 days at room temperature,⁸ and the mechanism is probably a further example of a nucleophilic 1,2-rearrangement (equation (5)), which is familiar in both organoborane and in organic peroxide chemistry.



Rearrangements of this type are accelerated by nucleophilic attack on the boron. If the diperoxyboranes, $\text{RB}(\text{OOR})_2$, are treated with a nucleophile such as pyridine or water, half the peroxide content is lost through a similar rearrangement of alkyl to peroxidic oxygen (equation (6)).¹⁰

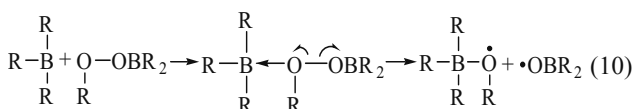
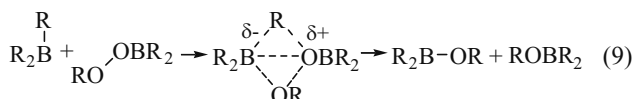
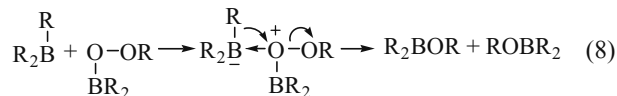


This rearrangement, with water as the nucleophile, complicated attempts to isolate hydroperoxides as the hydrolysis products, but intramolecular reduction can be avoided by treating the peroxide with a stronger oxidising agent such hydrogen peroxide or a peroxyacid, which is reduced preferentially.



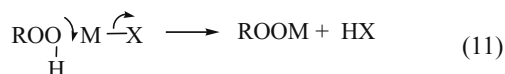
A similar intermolecular reaction can occur between RB and BOOR groups. This is probably in part a heterolytic reaction

(equation (8)), or at least a cyclic reaction with polar character (equation (9)), but it has also a homolytic component. The autoxidation of Me_3B or of Et_3B , when carried out in an NMR probe, shows a CIDNP effect for the BOCH_3 or BOCH_2CH_3 protons in the alkoxides which are formed,¹⁹ and the process shown in equation (10) has been suggested. The complex between the borane and alkoxyl radical would dissociate rapidly into an alkyl radical and the dialkylalkoxyborane. This homolysis is relevant to the use of organoboranes in the presence of oxygen as initiators of free radical reactions, as is discussed in Section 10.

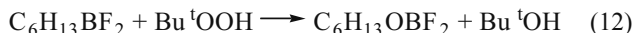


These intra- and inter-molecular oxidation-reduction reactions are responsible for the isolation of alkoxides rather than peroxides when autoxidations are carried out in more concentrated solutions (and it provides a method for preparing alcohols, see Section 8),¹¹ and this delayed recognition of the nature of the basic reaction.

A second route to alkylperoxymetallic compounds is by substitution by a peroxide nucleophile at the metal centre.

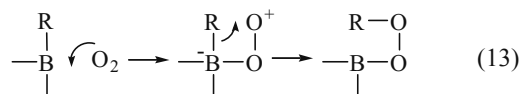


Organometallic peroxides of silicon,^{20,21} germanium, tin, and lead, such as $\text{Me}_3\text{SiOOCMe}_3$,²² $\text{Pr}_3\text{GeOOC}_{10}\text{H}_{17}$ ($\text{C}_{10}\text{H}_{17}$ = tetrahydro-1-naphthyl)²³, $\text{Bu}_2\text{Sn}(\text{OOBu}^t)_2$,²⁴ and $\text{Ph}_3\text{PbOOCPhMe}_2$ ²⁵ can be prepared by this method. Boron trichloride gives the peroxide $\text{B}(\text{OOBu}^t)_3$ as a crystalline solid melting at 15–18 °C, and $\text{B}(\text{OOBu}^n)_3$ as an oil, and $(\text{Bu}^t\text{OO})_2\text{OH}$, m.p. 38–42 °C was obtained from tetraacetylborate, but organoboron peroxides usually cannot be prepared by this method because of the nucleophilic B-to-O rearrangement of the organic group (e.g. equation (12)).²⁶



3 The mechanism of the autoxidation

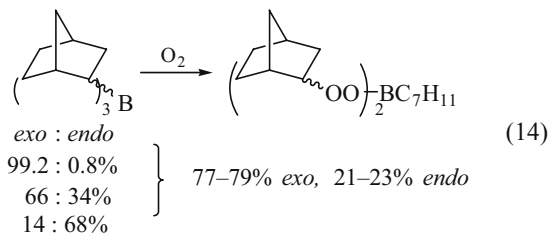
Hydrocarbon autoxidation involves a radical chain mechanism, but early attempts to inhibit organoborane autoxidation with the chain inhibitors which were then available, such as quinol, iodine, or methyl methacrylate, were unsuccessful, and the likely mechanism appeared to involve a nucleophilic 1,3-rearrangement of the alkyl group from boron to coordinated oxygen, after spin inversion (equation (13)).^{10,27-28}



Such a reaction should give retention of configuration if the rearranging group is chiral. In 1965, the optical resolution of 1-phenylethylboronic acid (**8**) by Matteson²⁹ made it possible

to test this, and the results are shown in Scheme 1, where the optical rotatory powers are normalised to the value for optically pure 1-phenylethanol. The complete racemisation in the 1-phenylethyl group, which is observed, is strong evidence against the rearrangement mechanism, and this was confirmed by the fact that the autoxidation is inhibited by galvinoxyl, a stable phenoxyl radical, which is a powerful chain breaker.³⁰ Inhibitors which have subsequently been found to be effective for other organoboranes include phenothiazine, copper dibutylidithiocarbamate, various phenols, and iodine.

Similarly the three mixtures of *exo*- and *endo*-norborylboranes shown in equation (14), gave the same diastereomeric mixtures of norbornylperoxyboranes, implying a common norbornyl (radical) intermediate, and again the reaction was inhibited by galvinoxyl.³¹

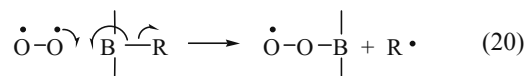


Scheme 1 Stereochemistry of the autoxidation of 1-phenylethylboronic acid.

Pokidova and Denisov assumed a preexponential factor for the attack of the peroxy radical at the boron centre of $A = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, to give the activation energies, which were analysed on the basis of the parabolic model, which considers the two intersecting vibrational energy parabolas of the breaking and forming bonds R–B and B–OOR.^{36,37} The reaction enthalpy, triplet repulsion between the entering and leaving group in the transition state, electronegativity of the B and O atoms, the force constants of the R–B and B–O bonds (and hence the bond dissociation energies), the presence of π -electrons in the vicinity of the reaction centre (*e.g.* benzyl), and steric factors, were all shown to contribute to the magnitude of the activation energy.

This mechanism is identical to that for the autoxidation of a hydrocarbon, HR replacing MR in the equations, and this led to the concept that metals often act as hydrogen equivalents in a broader context.³⁸ Support for the picture of a homolytic substitution at the boron centre is provided by Robert's observation of the hypervalent boron intermediate which is formed by the addition of an alkoxy radical to a B-alkylboronate formed from catechol, which is discussed below.

This leaves open the mechanism of the initiation process. Although hard evidence is lacking, this is usually assumed to be by an $\text{S}_{\text{H}}2$ reaction of triplet dioxygen at the boron centre (equation (20)).^{39,40}

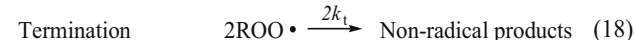
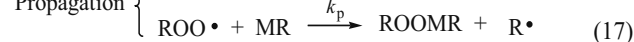
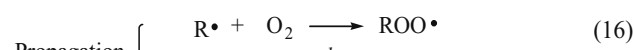
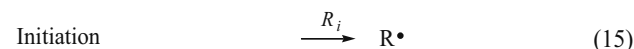


If galvinoxyl is added to the solvent before the borane, the induction period in air is greater than that under the same pressure of dioxygen, in accord with equation (20), but as the autoxidation progresses, the autoxidation products also act as more efficient initiators, perhaps by the mechanism shown in equation (10), and the rate of initiation becomes independent of the dioxygen concentration. A number of measurements of initiation rates have been made with different boranes³⁴ using phenyl- β -naphthylamine,²⁷ phenothiazine^{12,30} copper(II) NN-dibutylidithiocarbamate³⁰ TEMPO (tetramethylpiperidine *N*-oxyl),¹² various phenols,¹² galvinoxyl,^{33-35,41,42} or iodine,^{35,40,43,44} though the last does not give a clean reaction.^{35,45}

A radical chain mechanism for the autoxidation was therefore accepted, and this was confirmed by a kinetic analysis, but there is still some support for the insertion mechanism to apply particularly to some highly reactive organometallics,³² and electron transfer from oxygen may be involved with the more electropositive metals.

4 The kinetics of the autoxidation

By analogy with hydrocarbon autoxidation, the mechanism of organometallic oxidation would be as shown in equations (15)–(18).



By the steady state approximation, this leads to the kinetic equation

$$-\frac{d[\text{O}_2]}{dt} = k_p[\text{RM}] \left(\frac{R_i}{2k_t} \right)^{1/2} \quad (19)$$

The kinetics did follow this equation, and gave the rate constants, k_p , for bimolecular homolytic substitution ($\text{S}_{\text{H}}2$) at boron which are shown in Table 1.³³⁻³⁵ This explains why the inhibitors which had been used previously, were ineffective: for Bu_3B , for example, k_p is $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, and to compete with this, an inhibitor in, say, 5 mol% relative concentration, would have to have a reactivity 20 times this value.

Table 1 Rate constants ($\text{M}^{-1} \text{ s}^{-1}$) for the $\text{S}_{\text{H}}2$ reaction $\text{ROO} \cdot + \text{BR} \rightarrow \text{ROOB} + \text{R} \cdot$ at 303 K in octane

Structure	R = Bu ⁿ	R = Bu ^s	R = Bu ^t	R = PhCH ₂	R = PhMeCH
R ₃ B	2×10^6	8×10^4		5×10^6	
R ₂ BOR'	5×10^3	2×10^3			
R ₂ BOOR	3×10^4	1×10^4			
R ₂ BOBR ₂	3×10^5	7×10^4			
(RBO) ₃	1×10^3	5×10^4	3×10^4	1×10^8	4×10^6
RB(OR') ₂	small	4	0.3		

A thorough study of this initiation process is needed; it might provide information on the analogous initiation of autoxidation of hydrocarbons, which is more intractable to measurement, and on the precise origin of the radicals when organoboranes act as initiators of other radical reactions.

5 Ramifications

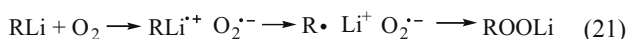
This identification of the nature of the products as peroxides, and of the mechanism as a free radical chain, carried some important implications, some of which were immediately apparent, but others which were appreciated only as work developed.

1. The organic derivatives of other metals similarly autoxidise or inflame in the air, hence these too, probably undergo a similar radical chain reaction with oxygen to give the organoperoxymetallic compound.
2. The parallel with hydrocarbon autoxidation suggested that other radicals which bring about an S_H2 reaction at hydrogen should also bring about an S_H2 reaction at boron.
3. Putting these two together, it seemed likely that a variety of electronegative radicals should take part in an S_H2 reaction at the metal centre in other organometallic compounds.
4. It should be possible to exploit this reactivity in designing new homolytic organic synthetic methods, both catalytically and stoichiometrically.
5. In a broader context, this concept of metals behaving as hydrogen equivalents might be relevant, not only in homolytic reactions, but also in heterolytic and pericyclic reactions, and again this analogy could be used in designing new reactions.³⁸

6 The autoxidation of organic compounds of other metals

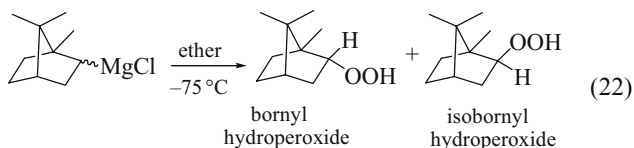
This picture of the mechanism of autoxidation of organoboranes suggested that it should apply also to the compounds of other metals which have a vacant low-lying orbital and a M-C bond which is weaker than a M-OOR bond. Indeed, the alkyl derivatives of many other Main Group metals are sensitive to autoxidation, and the (relatively limited) evidence which is available points again to a radical chain mechanism, though leaving open other possibilities in certain cases.

Walling and Bucker showed that if a dilute ethereal solution of an organolithium compound, RLi, was added during 43 min to oxygen-saturated ether ("inverse addition") at -75°C ,⁷ the product contained 36% of titratable peroxide, implying that the peroxide ROOLi is formed initially, but a substantial amount is then reduced by the parent RLi to give 2ROLi. A similar yield of peroxide (31%) is obtained using a hydrocarbon solvent at -75°C .⁴⁶ An attempt to inhibit the reaction with galvinoxyl was inconclusive because it reacts immediately with butyllithium, and has no effect on the subsequent autoxidation.⁴⁷ A chiral cyclopropyllithium compound reacts to give the corresponding alcohol with loss of stereospecificity;^{48,49} the interpretation is complicated by fact that the configuration of the product is the result of two separate steps, but it was concluded that free cyclopropyl radicals are involved in the autoxidations, perhaps through an electron-transfer process.



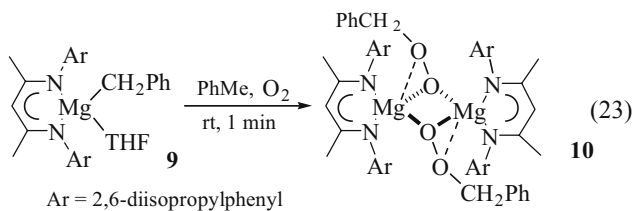
A dilute ethereal solution of a Grignard reagent, by the same technique of inverse addition at low temperatures, gave, after hydrolysis, the corresponding hydroperoxide (see Section 7),⁷ and similar results are obtained with a hydrocarbon solvent.⁴⁶ The Grignard reagent from *l*-bornyl chloride, which contains a mixture of bornyl- and isobornyl-magnesium chlorides,

gave a 56:44 mixture of bornyl and isobornyl hydroperoxides (equation (22)). The significance of the fact that what had been claimed in the literature to be the pure bornyl Grignard reagent gave the same mixture of hydroperoxides, was discounted on the grounds that the structure of the reactant had not been rigorously established.⁵⁰

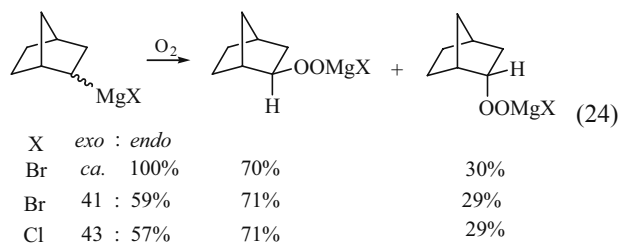


Cis- and *trans*-(1-bromo-2-methyl-2-phenylcyclopropyl) magnesium bromide react with oxygen to give alcohol with loss of stereospecificity, and the mechanism was assumed to involve an electron transfer process similar to that of equation (21).⁴⁹

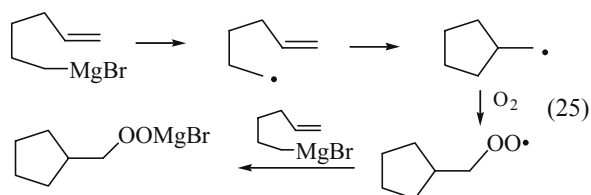
One organomagnesium peroxide has been isolated and its structure has been determined. The benzylmagnesium amide **9** reacts with oxygen in toluene to give the corresponding benzylperoxymagnesium amide **10**, with the structure shown. It co-crystallises with the corresponding benzyloxy compound which is formed by reduction of the peroxide (**10**) by its benzylmagnesium parent (**9**).⁵¹



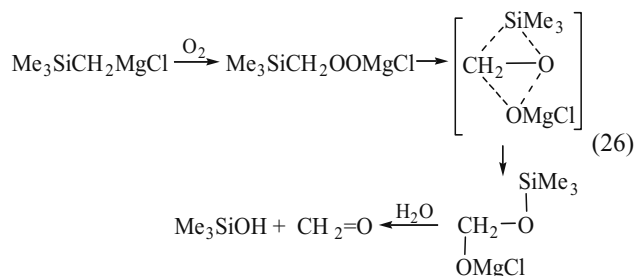
The evidence again points to a radical chain mechanism for the autoxidation (equations (15)–(18)). *endo*-Norbonylmagnesium bromide, or a mixture (*ca.* 60:40) of *endo*- and *exo*-norbonylmagnesium bromides or of chlorides (equation (24)), react with oxygen to give a similar mixture (*ca.* 30:70) of *endo*- and *exo*-norbonyl peroxides to that which was obtained with the norbornylboranes (equation (14)), suggesting a common norbornyl radical.⁵²



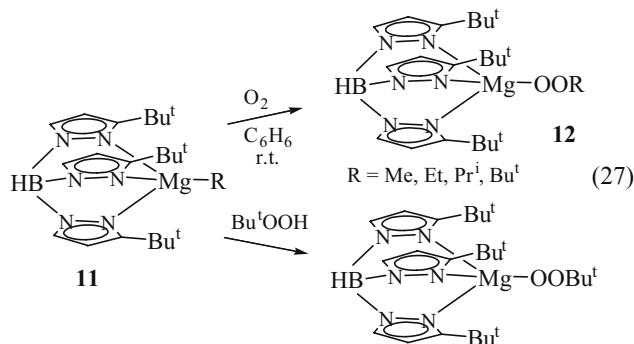
Again, the autoxidation of 5-hexenylmagnesium bromide at 0°C gives a substantial amount of the cyclopentylmethylperoxy product by the diagnostic cyclisation of the 5-hexenyl radical.⁵³



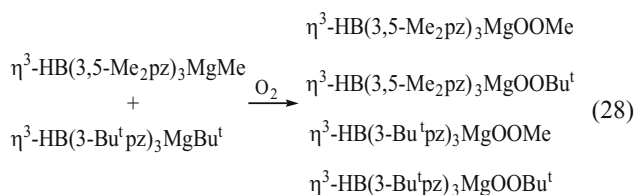
Autoxidation of trimethylsilylmethylmagnesium chloride gives trimethylsilanol and hexamethyldisiloxane as major products, which were suggested to arise from the rearrangement of the silyl magnesium peroxide (equation (26)), though rearrangement can also be envisaged of the intermediate $\text{Me}_3\text{SiCH}_2\text{OO}\cdot$ radical (see below).⁵⁴



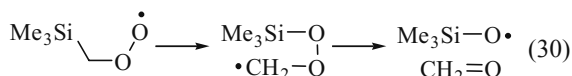
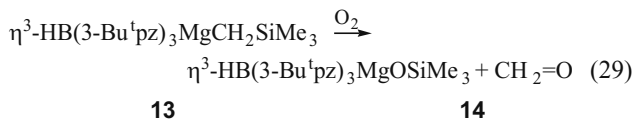
The tricyclic alkylmagnesium tris(pyrazolyl)hydroborato compounds **11** react with dioxygen in <10 min to give the corresponding peroxides **12** in quantitative yield, except when R = Me, when the reaction is slower (> 1 day), and the yield is lower (*ca.* 75%). When R = Bu^t, the same peroxide can be obtained from the reaction of *t*-butyl hydroperoxide with **11** (R = Me), and reduction of the magnesium peroxides with triphenylphosphine gives the corresponding alcohols. The good yields of the peroxides apparently result from the fact that the reduction of **12** by the parents **11** is slow because of steric hindrance.⁵⁵ The isotopically labelled peroxides, prepared with ¹⁷O₂, showed values of δ¹⁷O in the ranges of 102–183 and 323–427 (relative to H₂¹⁷O), which were assigned to the MgO¹⁷OR and Mg¹⁷OOR atoms respectively.



The autoxidation of **11**, R = Me, is inhibited by galvinoxyl, and the autoxidation of a mixture of magnesium derivatives with different pyrazolyl ligands and different alkyl groups as shown in equation (28), gives crossover products, consistent with the model of a radical chain mechanism.

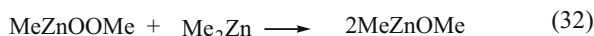


The autoxidation of the trimethylsilylmethyl derivative **13** gives the siloxyl derivative **14** and formaldehyde, and it was suggested that it results from a cyclic S_H2 reaction of the peroxy radical at silicon (equation (30)) rather than from the nucleophilic rearrangement which is shown in equation (26).



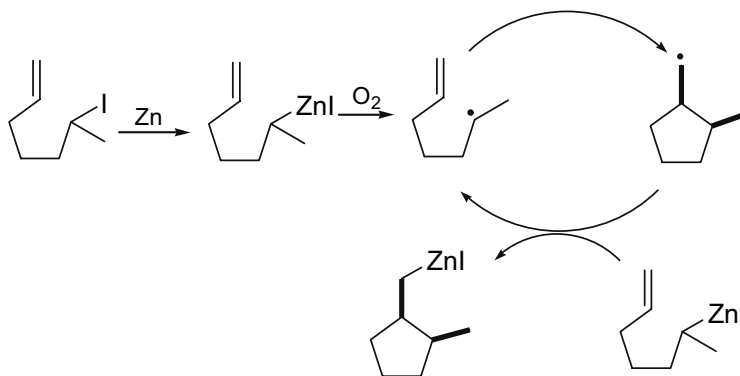
From time to time, various other reactions of Grignard reagents, even carbonyl addition, have been reported to show radical characteristics. It would be interesting to know whether these are dependent on traces of dioxygen for their initiation, and whether different (slower, heterolytic) reactions might not be observed if air is rigorously excluded.

Much attention has been paid to the organozinc compounds because of their familiarity in organic synthesis.² In solution, dimethylzinc reacts with dioxygen to give a product approximating to the formula of the methoxyperoxide, MeOZnOOMe, but only the later half of the reaction is inhibited by galvinoxyl. This suggests that the reaction of the first mole of oxygen gives the monoperoxide, but this is reduced by the dimethylzinc to give the methylzinc methoxide; this then takes up a second mole of oxygen. The second stage is established to be a radical chain reaction, and the first may well be also, but is not inhibited because galvinoxyl is not a powerful enough inhibitor to compete with the very reactive dimethylzinc.⁴⁷

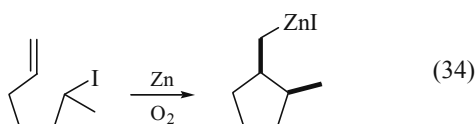


Diethylzinc at room temperature gives the diperoxide,⁵⁶ dibutylzinc gives the monoperoxide at –80°C,⁵⁶ and the diperoxide at 0°C⁴⁶ and room temperature.^{56,57} and butylzinc chloride gives BuOOZnCl.^{46,57} These reactions have been developed into a preparation of hydroperoxides (see Section 7).

Further evidence for a radical process is provided by the reaction of a secondary 5-hexenyl iodide with zinc to give *cis*-2-alkylcyclopentylmethylzinc iodide, which is dependent on the presence of a trace of dioxygen (equation 34). The crucial step is the S_H2 reaction of a primary alkyl radical at the zinc to displace the secondary alkyl radical (Scheme 2).⁵⁸

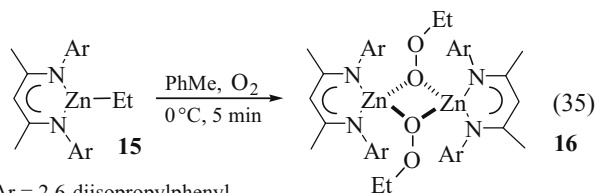


Scheme 2 Dioxygen initiation of the cyclisation of 1-methylpent-5-enylzinc iodide.



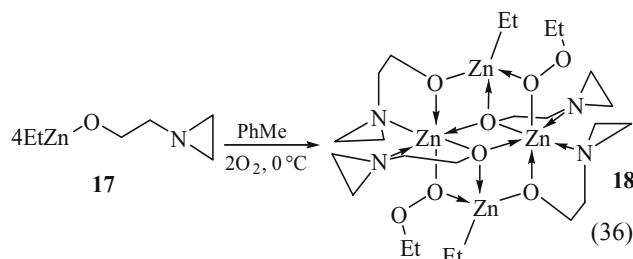
Recent work has led to the characterisation of organoperoxyzinc compounds by X-ray crystallography.

The complex **15** (equation (36)), formed by the reaction of diethylzinc with the 3-aminoimine, reacts with dioxygen to give the peroxide-bridged dinuclear complex **16** with the structure shown.⁵⁹

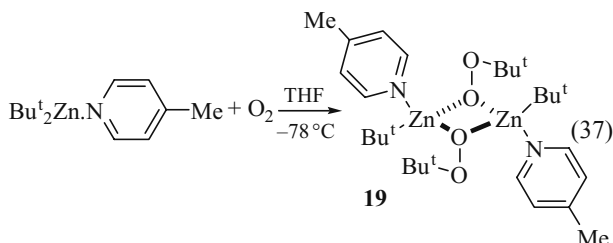


Ar = 2,6-diisopropylphenyl

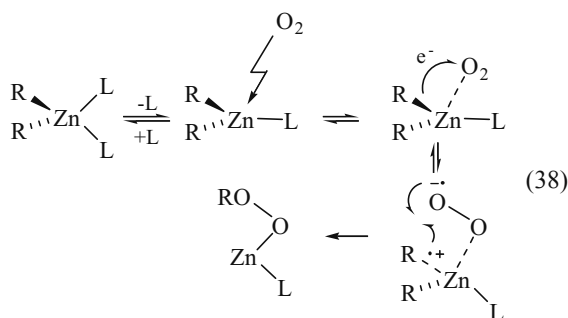
Ethylzinc 2-aziridineethoxide [EtZn(azol)] (**17**) reacts with dioxygen to give a complex, which can be represented as [EtOOZn(azol)]₂[EtZn(azol)]₂, with the structure **18**.⁶⁰



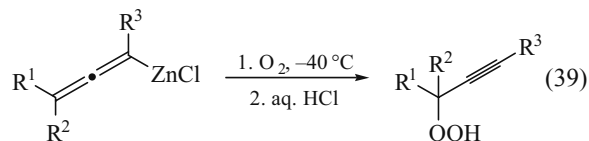
Autoxidation of Bu^t₂Zn in THF at -78 °C gave the alkoxide [Bu^tZn(μ-O^tBu)(THF)]₂, but autoxidation in the presence of 4-methylpyridine at -45 °C gave the peroxide [Bu^tZn(μ-OOBu^t)(py-Me)]₂ (**19**).³²



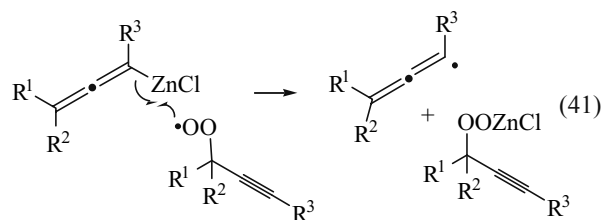
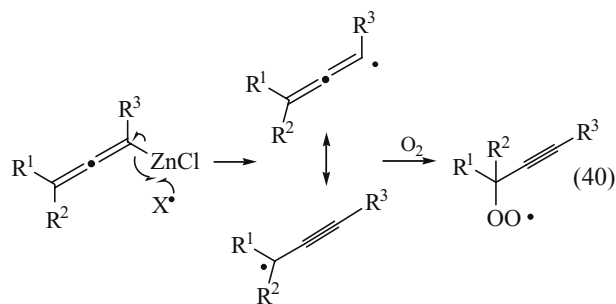
It is suggested that the autoxidation of the first R-Zn bond in the methylpyridine complex does not involve a radical chain, but rather an electron transfer process. A weak interaction with zinc changes the electronic structure of the dioxygen, then electron transfer gives a solvent-caged radical pair, which then reacts, with triplet-singlet crossing, to give the peroxide (equation (38)). At higher temperature, the alkyl radical may escape the cage, to initiate the radical chain process. TEMPO (tetramethylpiperidine nitroxyl) had no effect on the reaction.³²



Allenic zinc compounds react with dioxygen to give propargylperoxyzinc products, and thence, by hydrolysis, the corresponding hydroperoxides (see Section 7) as shown in equation (39).⁶¹

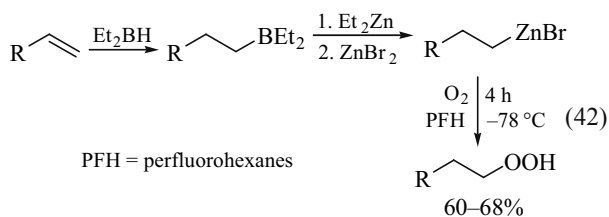


The mechanism of the reaction has not been established, but it can reasonably be represented as a conventional S_H2 attack by a peroxy radical at zinc (equations (40) and (41)). It would be difficult to reconcile a direct insertion of the dioxygen into the Zn-C bond, as in equation (38), with the fact that an allenyl-to-propargyl rearrangement occurs during the reaction. This argument would fail if there is a rapid metallotropic equilibrium between the allenyl- and propargyl-zinc compounds, but the NMR spectrum shows only the allenyl structure.⁶²



Klement and Knochel appear to have been the first to use perfluoroalkanes as solvents for autoxidation of organometallic compounds.^{63,64} This has the dual advantage of giving a much higher concentration of dioxygen, so minimising reduction of MOOR by MR and thereby making it possible to reduce drastically the volume of solvent, and also of reducing the explosion hazard which is very real when using large volumes of a solvent such as ether under pure dioxygen in the presence of an organometallic compound, which may be spontaneously inflammable even in air. Anyone intending to carry out autoxidation reaction of organometallics is strongly advised now to use fluorinated solvents.

In perfluorohexanes, the alkylzinc halides give better yields of peroxides than do the dialkylzincs.⁶³ This reaction provides a route to hydroperoxides by the hydrozincation or carbocation of alkenes, or by the boron/zinc exchange shown in equation (42) (see Table 4, Section 7).



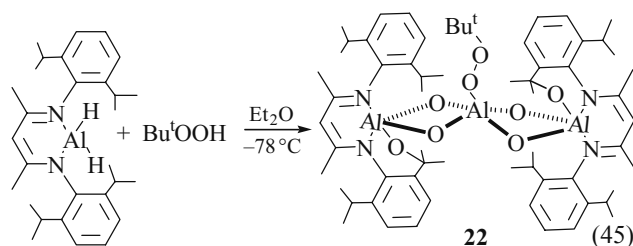
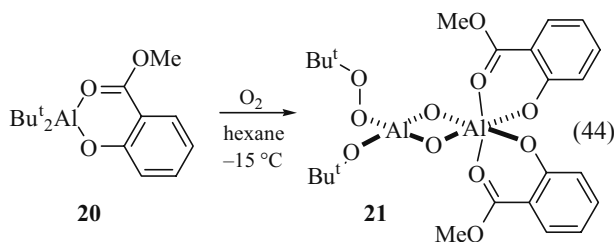
These autoxidation reactions are relevant to the use of organozinc compounds as initiators for homolytic reactions (see Section 10).

Little work has been reported on the autoxidation of organocadmium compounds but it is clear that their behaviour is similar to that of the analogous magnesium and zinc compounds. Dimethylcadmium in ether at room temperature absorbs one mole of dioxygen in about 100 min to give MeCdOOME.^{65,66} Diethyl- and dibutyl-cadmium are much more reactive and give the diperoxides Cd(OOR)₂,^{46,65} and octyl- and benzyl-cadmium chlorides give good yields of the peroxides ROOCdCl.⁴⁶ The reaction of dimethylcadmium is inhibited by galvinoxyl,⁴⁷ and it is assumed that the mechanism is that of the radical chain of equations (15)–(18).

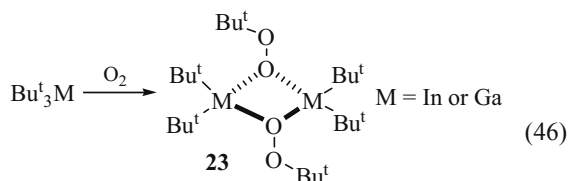


Organoaluminum compounds (e.g. Me₃Al, Et₃Al, BuAlCl₂) are usually very reactive towards oxygen, but the yield of peroxide is usually less than 10% because the products are reduced by the reactants.^{46,67} After Me₃Al has absorbed 0.5 mol of dioxygen, the reaction is inhibited by galvinoxyl, thus at least this stage of the reaction follows the radical chain mechanism.⁴⁷

Autoxidation of the 4-coordinate methylsalicylate complex Bu₂Al(mesal) (**20**) gives a crystalline dinuclear peroxy complex, which X-ray diffraction showed to have the structure shown in **21**,⁶⁸ and a further *t*-butylperoxy aluminium compound (**22**) has also been isolated from the reaction of an aluminium hydride with *t*-butyl hydroperoxide.⁶⁹ It is interesting that the formation of **22** involves the hydrogen atoms at two of the isopropyl groups, which would be expected to have a high homolytic reactivity.



Autoxidation of trimethylindium and trimethylgallium gives the monoperoxides Me₂MOOME,⁷⁰ and tri-*t*-butylindium⁷¹ and tri-*t*-butylgallium,⁷² at -78°C, give the isostructural dimeric peroxides [Bu₂MOOBu^t]₂ (**23**).

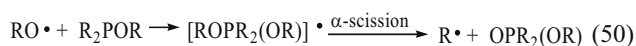
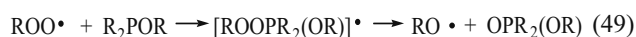
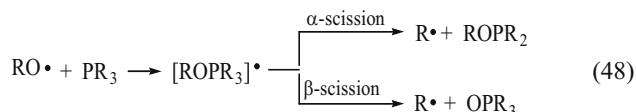
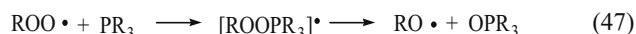


It is interesting that tri-*t*-butylindium is reported to react with pyridine *N*-oxide to give Bu^t₂InOBu^t as the major product, which then reacts slowly with the *N*-oxide to give small

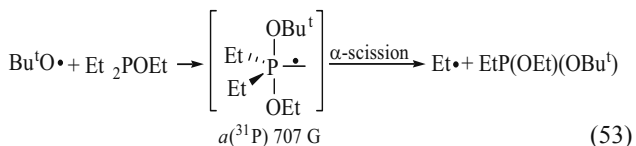
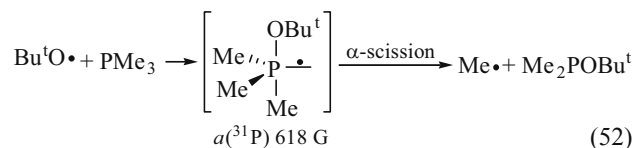
quantities of the peroxide **23** (M = In). There appears to be no precedent for the formation of a peroxide by this type of reaction, and further adventitious autoxidation of Bu^t₃In would not appear to be ruled out.⁷²

The autoxidation of phosphines, stibines, and bismuthines is complicated by the existence of the M^{III} and M^V oxidation states, but has the common feature with the other metals in that it involves attack at the heteroatom by an alkylperoxy radical.

The salient features of phosphine autoxidation were elucidated by Buckler in 1962.⁷³ The reaction of tributylphosphine is inhibited by diphenylamine and quinol, and the principal products are the phosphine oxide, Bu₃PO, and phosphinate, Bu₂P(O)OBu. The mechanism is shown in equations (47)–(51).⁷⁴



Phosphoranyl radical intermediates, R_n(OR')_{4-n}P•, have since been identified by ESR spectroscopy.⁶⁸ They have a trigonal bipyramidal structure, with the unpaired electron as a phantom ligand in an equatorial, largely sp², orbital, and they can undergo α-scission to give the radical R• or β-scission to give the radical R'•; under normal conditions, the former process is the more important (e.g. equations (52) and (53)), though β-scission can occur in suitable structures.



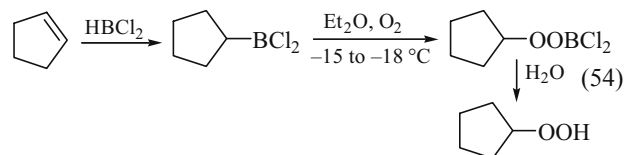
The autoxidation of alkylarsines probably follows a similar basic mechanism, and arsenanyl radicals, R₃(OR')As• have been detected by ESR spectroscopy.⁷⁵ The autoxidation of stibines and bismuthines can be inhibited by radical scavengers such as galvinoxyl and phenothiazine,⁷⁶ and it has been shown by ESR spectroscopy that *t*-butoxyl radicals react with trialkyl-stibines and -bismuthines, to displace the alkyl radicals. Me₃Sb gives, after hydrolysis, methanol as the main organic product, and Et₃Sb gives ethanol and acetaldehyde. Me₃Bi and Et₃Bi give the corresponding alcohols, but also the ethers, ROR, and dialkyl peroxides, ROOR, and a mixture of Me₃Bi and Et₃Bi gives also the mixed ethers and peroxides, MeOEt and MeOOEt. The detailed mechanisms are far from being understood, but clearly these autoxidations of stibines and bismuthines again follow radical chain processes involving the alkylperoxy radicals.

7 The preparation of hydroperoxides

The autoxidation of boranes has been used as a route to alkyl hydroperoxides, particularly the secondary alkyl hydroperoxides which may be difficult to prepare by other methods.⁷⁷ The organoboranes are often conveniently prepared by hydroboration of alkenes, then, after autoxidation, the hydroperoxides are liberated with a peroxyacid or with hydrogen peroxide (Table 2). The hydroperoxide and alcohol can be separated through the potassium salt of the hydroperoxide.⁷⁸ These reactions were devised at a time before the advantages of using fluorocarbon solvents had been recognised, and a change to these solvents should be an improvement, if only on safety grounds.

With a trialkylborane as the reactant, this reaction is wasteful of one group R; this can be avoided by using instead

the alkylchloroborane complex $\text{RBCl}_2 \cdot \text{OEt}_2$ in ether; the complexation moderates the rate of autoxidation and reduces the degree of reduction of BOOR by BR . The peroxyboranes can then be hydrolysed with water to give the hydroperoxide in good yield,⁴⁰ e.g.:



The hydroperoxides which were prepared by this method, with the yields (by titration), are 1-hexyl 94%, 3-hexyl 93%, 2-methyl-1-pentyl 84%, cyclopentyl 91%, cyclohexyl, 93%, and norbornyl 91%.

Table 2 Hydroperoxides prepared by autoxidation of trialkylboranes

Alkene	Borane R_3B	Work-up	ROOH^a (yield/%)	ROH^a (yield/%)	Ref.
$\text{C}_2\text{H}_5\text{CH}=\text{CH}_2$	$(\text{C}_4\text{H}_9)_3\text{B}$	H_2O_2	92 ^b		78
$n\text{-C}_6\text{H}_{13}\text{CH}=\text{CH}_2$	$(n\text{-C}_8\text{H}_{17})_3\text{B}$	H_2O_2	40.7 ^a 81 ^b	20.6 ^a	77 78
$n\text{-C}_8\text{H}_{17}\text{CH}=\text{CH}_2$	$(n\text{-C}_{10}\text{H}_{21})_3\text{B}$	H_2O_2	51 ^b		77
$n\text{-C}_9\text{H}_{19}\text{CH}=\text{CH}_2$	$(n\text{-C}_{11}\text{H}_{23})_3\text{B}$	H_2O_2	47.3 ^a	47.6 ^a	77
$\text{MePrC}=\text{CH}_2$	$(\text{MePrCHCH}_2)_3\text{B}$	H_2O_2	90 ^b		78
$\text{EtBuC}=\text{CH}_2$	$(\text{EtBuCHCH}_2)_3\text{B}$	MeCO_3H	36 ^a	33 ^a	77
$\text{PhCH}=\text{CH}_2$	$(\text{PhCH}_2\text{CH}_2)_3\text{B}$	MeCO_3H	38 ^a	39 ^a	77
$\text{MePhC}=\text{CH}_2$	$(\text{MePhCHCH}_2)_3\text{B}$	H_2O_2	53 ^a	40 ^a	77
$\text{MeCH}=\text{CHMe}$	$(\text{MeEtCH})_3\text{B}$	H_2O_2	91 ^b		78
^c	$(\text{PhCH}_2)_3\text{B}$	MeCO_3H	30 ^a	33 ^a	77
		H_2O_2	95 ^b		78
		H_2O_2	91 ^b		78
		H_2O_2	53.4 ^a 95 ^b	53.4 ^a	77 78
		H_2O_2	84 ^{b d}		78
		H_2O_2	49 ^a	46.5 ^a	77
		H_2O_2	47.3 ^a	46.2 ^{a e}	77
		PhCO_3H	58 ^a	35 ^f	77

^a Yields of isolated product, based on alkene, which was hydroborated with $\text{H}_3\text{B} \cdot \text{NEt}_3$ then treated in hexane with dioxygen, usually at 0°C .

^b Yields by titration, based on alkene, which was hydroborated with $\text{H}_3\text{B} \cdot \text{THF}$ then treated with oxygen at -78°C .

^c From PhCH_2MgCl and $\text{BF}_3 \cdot \text{OEt}_2$.

^d 80% *exo*, 20% *endo*.

^e 54.9% 1-indanol, 34.7% 2-indanol, 10.5% 1-indanone.

^f Based on borane.

Table 3 Hydroperoxides prepared by the autoxidation of Grignard reagents

R MgX	ROOH^a	R MgX	ROOH^a
Et MgCl	EtOOH 57	$\text{Me}_3\text{C MgCl}$	Me_3COOH 86
Et MgBr	EtOOH 28	$\text{Me}_2\text{EtC MgCl}$	Me_2EtCOOH 92
Bu MgCl	BuOOH 57	HexMeCH MgCl	HexMeCHOOH 91
PhCH ₂ MgCl	PhCH ₂ OOH 30		90
	66, 65 ^b		30
BuLi	BuOOH 36	Bu_2Zn	BuOOH 48
		$[(\text{CH}_2)_3\text{MgCl}]_2$	$[(\text{CH}_2)_3\text{OOH}]_2^b$

^a Yields by titration. ^b Ref.⁵⁷

Table 3 gives the yield of hydroperoxides (by titration) obtained by autoxidation of Grignard reagents by Walling's method of reverse addition in ether at -75°C .⁷

Hydroperoxides prepared by Klement and Kochel's method of autoxidation of alkylzinc bromides in perfluorohexanes (equation (42)) are shown in Table 4.⁶⁴

The propargyl hydroperoxides which have been prepared by the autoxidation of allenic zinc compounds (equation (39)), are shown in Table 5.⁶¹

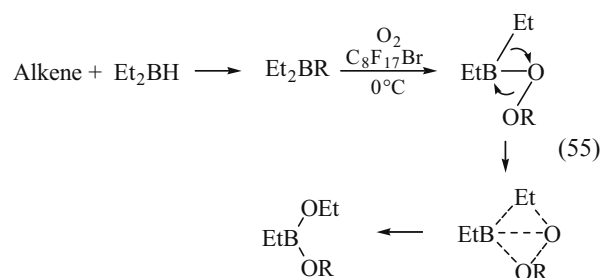
Table 4 Hydroperoxides obtained from autoxidation of alkylzinc bromides in perfluorohexanes

Alkene	Hydroperoxide	Yield/%
		64
		62
		67
$n\text{-C}_6\text{H}_{13}\text{CH}=\text{CH}_2$	$n\text{-C}_8\text{H}_{17}\text{OOH}$	85
		69
		69
		62
		68
		61
		60
		58

8 The preparation of alcohols

The autoxidation of organometallic compounds with a restricted supply of oxygen provides a direct route to alcohols, which may be useful as an alternative to oxidation with a peroxide or with an amine oxide. If the oxygenation in THF is continued until 1.5 mol. of O_2 are absorbed per mol. of trialkylborane,⁷⁹ then the product is hydrolysed with NaOH, the alcohols can be obtained in 90–99% yield from olefins by hydroboration/autoxidation. The nature of the products differs from than obtained with a peroxide or amine oxide in that, as a radical is involved in the autoxidation, stereospecificity is lost (e.g. in norbornene \rightarrow norbornanol). Examples are 1-butene \rightarrow 94% butanol (95% primary, 5% secondary), isobutene \rightarrow 98% isobutyl alcohol, cyclopentene \rightarrow 95% cyclopentanol, and norbornene \rightarrow norbornanol (86% *exo*, 14% *endo*).

The diethylboranes, Et_2BR , react readily with dioxygen in $\text{C}_8\text{F}_{17}\text{Br}$ at 0°C , to give good yields of alcohols ROH, with, remarkably, retention of configuration in the group R, because the Et-B group is more reactive towards dioxygen than is the R-B group. The EtOOB group which is formed is then reduced by a 1,2-rearrangement in which R is more mobile than is Et, to give ROH without the radical $\text{R}\cdot$ being an intermediate.⁶⁴ The reaction is tolerant of a variety of functional groups, as shown in Table 6, which gives the yield of alcohols which is obtained from the original alkenes.



Most boronic esters do not undergo autoxidation. The boronates derived from catechol, however, do react with dioxygen but the solution blackens and the yield of hydroperoxide is low.⁴⁰ Autoxidation, however, occurs smoothly in the presence of triethylamine (12 h at room temperature), but the products are now alkoxyamines rather than peroxides (Table 7).^{80,81} Reduction of the alkoxyamines with zinc in acetic acid then gives the alcohols. The function of the amine is intriguing. The radical nature of the reaction is confirmed by the fact that the boronate from norcarene gives a mixture of the bicyclic and the monocyclic alcohols in the ratio of 1:2 (equation (56)),

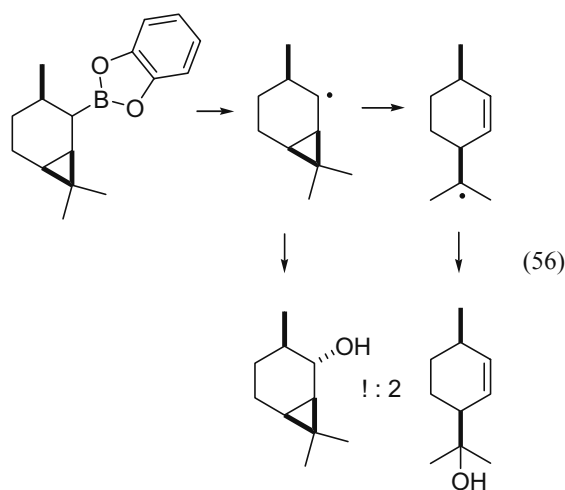
Table 5 Propargyl hydroperoxides obtained from autoxidation of allenylzinc bromides in perfluorohexanes^a

Allenylyzinc	Propargyl hydroperoxide	R	Yield/%
		Bu	92
		Bu ^s	54
		Bu ^t	81
		Bu	53
		Bu ^s	75
		Bu ^t	50
		Bu	84

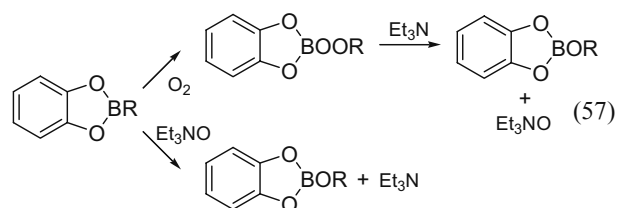
^aThe organozinc bromide in THF is added during 2 h to perfluorohexane saturated with oxygen at -78°C .

Table 6 Alcohols obtained from autoxidation of alkyldiethylboranes in $C_8F_{17}Br$

Alkene	Alcohol	Yield/%
		81
		89
		85
		71
		88
		91
		75
		71
		95
		81
		75
		82
		61
		71
		65
		79



It is suggested that the amine is oxidised by the peroxyborane to the amine oxide, which then (stereospecifically) oxidises the alkylborane to alkoxyborane, with regeneration of the amine. This special reactivity of the catechol boronates is discussed below.



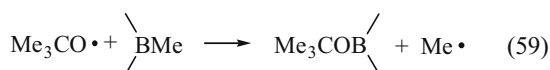
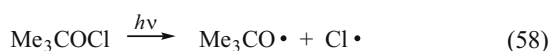
9 S_H2 at boron by other oxygen-centred radicals

This discovery that autoxidation involved a rapid S_H2 reaction at boron suggested that other electronegative radicals might

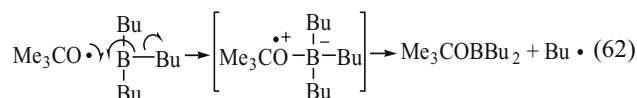
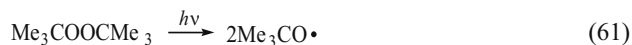
Table 7 Alcohols obtained from autoxidation of catecholboranes in the presence of triethylamine

Alkene	Alcohol	Yield/%
		85 (10:1)
		59 (12:1)
		64 (9:1)
		71 (11:1)
		46 (4:1)
		81 (2:1)
		62

do the same thing, and the reaction of *t*-butyl hypochlorite with trimethylboroxine under UV irradiation appeared to be such an example involving the *t*-butoxyl radical in a chain reaction.



This was confirmed by carrying out the alkoxydemethylation in a non-chain sense by photolysing di-*t*-butyl peroxide in the presence of an alkylborane in an ESR cavity, when the spectrum of the alkyl radical was observed.^{82,83}

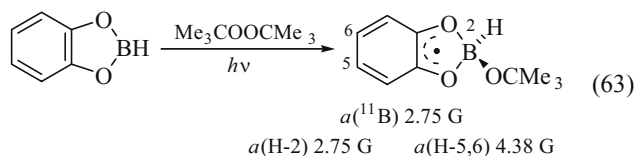


By causing the borane to compete with cyclopentane for reaction with *t*-butoxyl radicals, the ratio of the concentrations of the butyl and cyclopentyl radicals can be measured from the relative intensities of the ESR spectra, and the rate constants for *t*-butoxydealkylation at boron can be obtained.⁸⁴

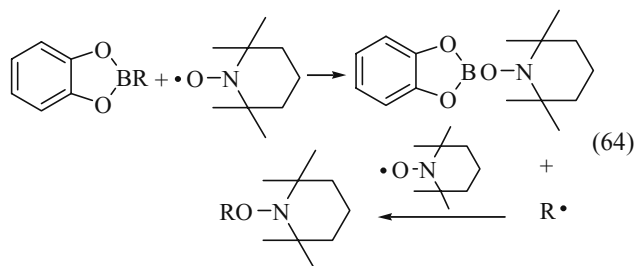
This technique provides a general method for observing the ESR spectrum of alkyl radicals, requiring no special equipment such as a van der Graaf generator. It permits the presence of a wide variety of functional groups, and can be extended to the use of other metals, and made it possible to observe for the first time the spectra of many short-lived radicals.

The presence of an intermediate was suspected, and was detected by UV spectroscopy in 1977 in the reaction of *t*-butoxyl radicals with triphenylborane, but its ESR spectrum could not be observed: if it were formed, its lifetime was too short.⁸⁵ The alkylboronates derived from catechol, however,

have special properties: the lone electron pairs on oxygen are involved in the aromatic electron system and are less available for interaction with boron, and if a radical adds to the boron, the system is stabilised by delocalisation over the catechol moiety. The result is that, whereas simple boronates have a low reactivity towards alkoxy radicals, the catecholboranes show a high reactivity, and the perboryl radical intermediates which are formed are stabilised, and their ESR spectra were observed by Roberts in 1986, *e.g.* equation (63).⁸⁶


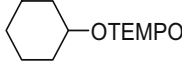

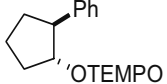

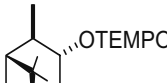

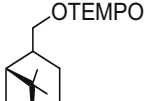




This special reactivity of the catecholboranes has enabled a new route to hydroxylamines to be developed. Though trialkylboranes do not react with TEMPO, the catecholboranes do; two molar equivalents of TEMPO are needed, the first to carry out the S_H2 reaction at boron, and the second to trap the alkyl radical that is displaced. In Table 8, the yields are based on the parent alkenes which are hydroborated with catecholborane in refluxing THF, then treated with ethanol and TEMPO in the presence of dimethylpropyleneurea at room temperature.⁸¹



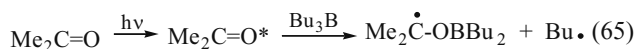
A variety of other synthetic reactions which exploit this reactivity of catecholboranes have recently been developed.^{6,87,88}

Table 8 Alkoxyamines obtained from the reaction of catecholboranes with TEMPO

Alkene	Alcohol	Yield (%)
		87
		dr 89:11 ^a 71
		dr 97:3 ^a 82
		dr 91:9 ^a 57
		64

^aThe major diastereomer is shown

Ketones in the $n \rightarrow \pi^*$ triplet state often show reactions similar to those of alkoxy radicals, and will abstract hydrogen which is bonded to carbon. They will similarly bring about an S_H2 substitution at a boron centre (*e.g.* equation (65)). The ESR spectra of the two resultant radicals can be observed, and the rate constant of the particular example in equation (65) is $7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.⁸⁹



A variety of other electronegative radicals have been shown to bring about the S_H2 reaction at a boron centre, often both in a chain and a non-chain sense. For the non-chain reactions, the displaced alkyl radical has usually been observed by ESR spectroscopy. These reactions have been reviewed elsewhere,^{3,90} and will not be considered further here.

10 Organoboranes as radical initiators and radical reagents

Apart from initiating their own autoxidation, organoboranes in the presence of a trace of air or dioxygen can initiate other homolytic chain reactions of boranes, or of non-boron reagents. The initiating radicals could be of at least four different types.

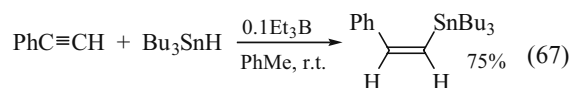
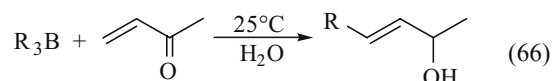
1. The same radicals, perhaps the radicals $\text{R}_2\text{BOO}\cdot$ and $\text{R}\cdot$ (equation (20)), which may initiate autoxidation.
2. The radicals $\text{R}\cdot$ and $\text{ROO}\cdot$ which propagate the autoxidation (equations (16) and (17))
3. The radicals which are formed when the peroxyborane reacts with an alkylborane, perhaps $[\text{R}_2\text{BOR}]\cdot$ and $\cdot\text{OBR}_2$ by reaction (10).
4. The radicals $\text{R}_2\text{BO}\cdot$ and $\cdot\text{OR}_2$ from the unimolecular homolysis of the $\text{BO}-\text{OR}$ bond in the peroxide.

At or below room temperature, the first three processes may be involved, but the last one is probably relevant only at higher temperature. In the earliest work on borane autoxidation, Grummitt showed that partially oxidised butylboronic anhydride and dioxygen would initiate the polymerisation of vinyl acetate at 70°C ,²⁷ and there are many subsequent examples of the use of the system for initiating homolytic polymerisation.⁹¹⁻⁹³

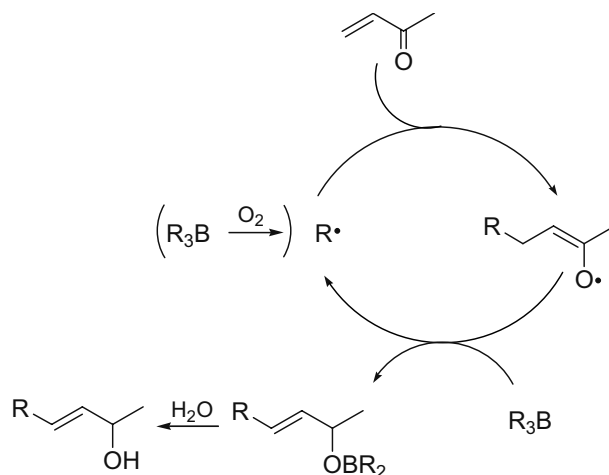
Boranes, in the presence of a trace of air or dioxygen, are now widely used as radical initiators, but despite this growing importance, no attempt appears to have been made to determine which particular initiation process is involved.

The boranes have the major advantage over the conventional initiators such as benzoyl peroxide or AIBN, which are effective only above about 80°C , that they can be used at low temperature (frequently -78°C), permitting reactions with heat-sensitive materials, and with an improvement in stereoselectivity. A further advantage is that the reactions with a borane reagent may provide an alternative to the reactions involving organotin compounds, which carry concerns over organotin toxicity.

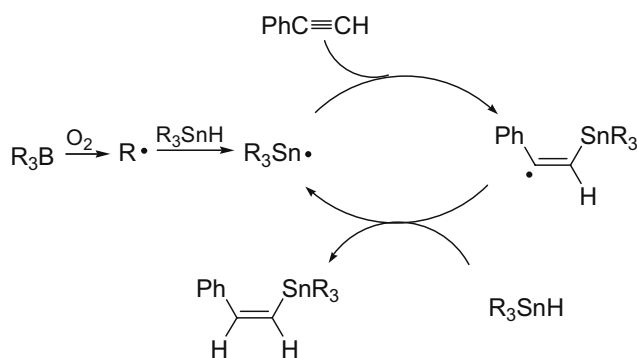
Borane-initiated reactions have been reviewed recently elsewhere,^{3,4} hence only two simple examples are given in equations (66) and (67), with the mechanisms in Schemes 3 and 4, one with a borane reagent, and the other with a non-borane reagent, to illustrate the principles involved.



The use of organozinc compounds as initiators is increasing. Again, the detailed mechanism by which they react has not



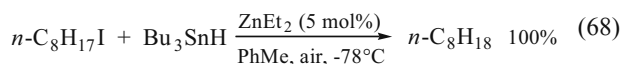
Scheme 3 Homolytic mechanism of the alkylboration of an enone.



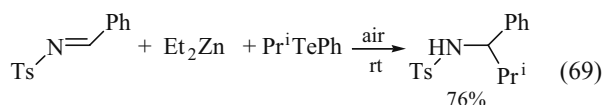
Scheme 4 Organoborane initiation of hydrostannation of an alkyne.

been investigated, and, as yet, no substantial difference between their performance and that of the boranes appears to have been reported. The topic has recently been reviewed,⁹⁴ and only two examples are given here to illustrate the principles.

In the first (equation (68)), diethylzinc reacts with dioxygen to give radicals which initiate the hydrostannolysis of an alkyl iodide (Scheme 5).⁹⁵

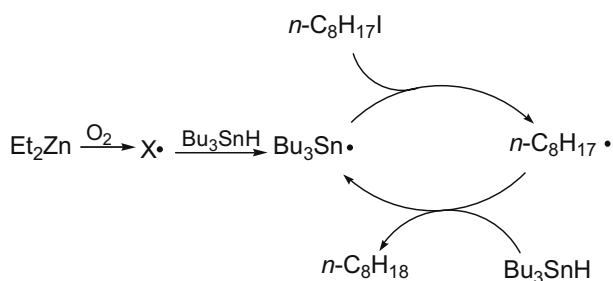


In the second, diethylzinc acts both as an initiator and, twice, as stoichiometric reagent, the second occurrence involving an $\text{S}_{\text{H}2}$ reaction at zinc to displace a PhTe radical (equation (69)) and Scheme 6.⁹⁶ The reaction with dimethylzinc was much slower, and this was ascribed to a lower rate of initiation.

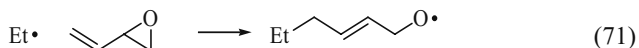
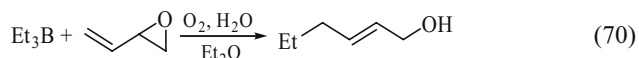


None of the other autoxidisable organometallics, which would be expected to act similarly as initiators, has yet been studied.

The development of organoboranes as stoichiometric radical reagents in synthesis results again in part from concerns about the toxicity of the organotin compounds which often give equivalent reactions. The principle is illustrated by the example of the addition of a borane to an unsaturated epoxide (equation (70)); oxygen initiation produces the ethyl radical, which reacts with epoxide to give an oxyl radical (equation (71)), which then brings about an $\text{S}_{\text{H}2}$ reaction with the borane to displace an ethyl radical, which continues the chain (equation (72)).



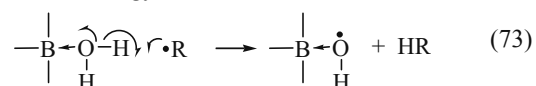
Scheme 5 Organozinc initiation of the hydrostannolysis of an alkyl iodide.



Again, this topic has been reviewed recently^{3,5} and will not be covered further here.

11 Current developments

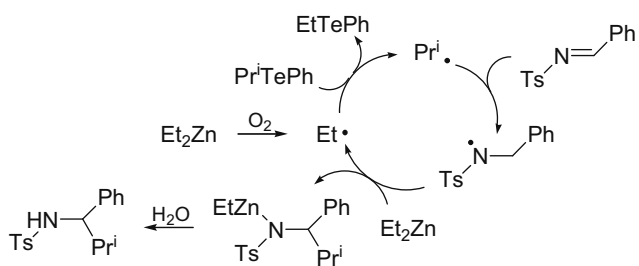
The homolytic reaction of boranes with oxygen, and, more generally, the rapid $\text{S}_{\text{H}2}$ reaction at the boron centre, now provides valuable tools for the synthetic chemist. A remarkable new development, which promises to widen the scope of these reactions, is the accidental discovery that alkyl radicals can bring about an $\text{S}_{\text{H}2}$ reaction at hydrogen in ligated water, which might be expected to be ruled out by the high dissociation energy of the O–H bond.



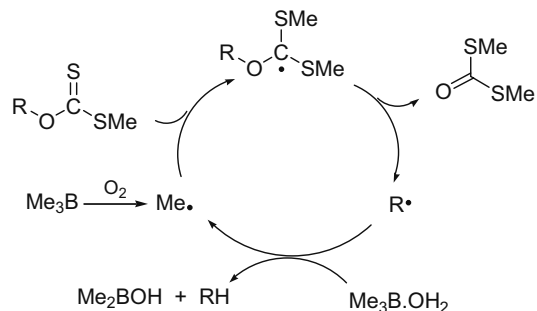
Wood was following a report by Barton that triethylborane reacted with an alkyl xanthate to give some alkane, and showed by deuterium labelling, that an alkyl radical abstracted hydrogen, not from the ethyl group or the solvent, but from adventitious water which was ligated to the borane. The reaction worked with primary, secondary, and tertiary alkyl radicals, and also with trimethyl- and tributyl-borane, trimethylborane being the best. The proposed mechanism is shown in Scheme 7.⁹⁷

Gaussian-3 calculation showed that, on coordination to Me_3B , the dissociation energy of the H–O bond was reduced from 116 to 86 kcal mol⁻¹, though apparently not when water coordinates to trimethylaluminium.

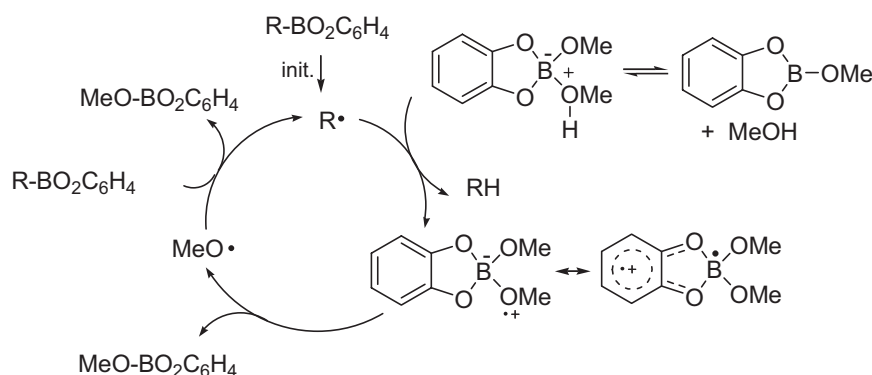
Renaud discovered a similar process with the catechol boranes. An attempt to allylate a *B*-alkyl catecholborane with a phenyl allyl sulfone gave a substantial amount of the alkane, and the source of the hydrogen was traced to methanol which was used in preparing the borane (equation (74)).⁹⁸



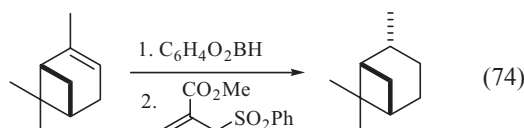
Scheme 6 Diethylzinc as an initiator and reagent.



Scheme 7 Reduction of a xanthate by a borane.



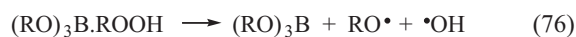
Scheme 8 Reduction of a B-alkyl catecholborane to an alkane.



The reaction was shown to be dependent on the presence of a trace of dioxygen, and deuterium labelling showed that the reducing hydrogen atom was derived from the alcohol. The proposed mechanism is shown in Scheme 8.

Newcomb has measured the rate of abstraction of hydroxyl hydrogen by an alkyl radical from $E_3B.OH_2$ by the radical clock technique, and obtained a rate constant of $2.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, which is about 100 times faster than that from Et_3SiH , and about 100 slower than that from Bu_3SnH . The equilibrium constant for the formation of the hydrate of the trialkylborane, however, does not appear to be known.⁹⁹

This opens up exciting possibilities and raises the question of the how far the principle applies to different Lewis acids and bases. Is it relevant, for example, to the apparent weakening for the peroxide bond when a peroxyborane reacts with an organoborane as shown in equation (10)? It might even provide an answer to the mechanism of the commercially important but enigmatic Bashkirov reaction,^{100,101} in which the presence of boric oxide during the autoxidation of an alkane, diverts the reaction from forming ketone and alcohol into giving principally the alcohol. A reaction analogous to that of equation (10),¹⁰² as shown in equations (75)–(78), now seems an attractive possibility.



These recent developments might yet be one of the most valuable legacies which can be traced back to Frankland's fuliginous flame.

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