EPR and preparative studies of 5-endo cyclizations of radicals derived from alkenyl NHC-boranes bearing tert-butyl ester substituents

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Abstract: Radical H-atom abstraction from a set of N-heterocyclic carbene (NHC) complexes of alkenylboranes bearing two tert-butyl ester substituents was studied by EPR spectroscopy. The initial boraallyl radical intermediates rapidly ring closed onto the O-atoms of their distal ester groups in 5-endo mode to yield 1,2-oxaborole radicals. Unexpectedly, two structural varieties of these radicals were identified from their EPR spectra. These proved to be two stable rotamers in which the carbonyl group of the tert-butyl ester was oriented towards and away from the NHC ring. These rotamers were akin to the s-trans and s-cis rotamers of α,β-unsaturated carbonyl compounds. Their stability was attributed to the quasi-allylic interaction of their unpaired electrons with the carbonyl units of their adjacent ester groups. EPR spectroscopic evidence for two rotamers of the analogous methyl ester containing NHC-oxaborole radicals was also obtained. An improved synthetic procedure for preparing rare NHC-boralactones was developed involving treatment of the alkenyl NHC-boranes with AIBN and tert-dodecanethiol.

INTRODUCTION
N-Heterocyclic carbene boryl radicals (hereafter NHC-boryl radicals) are emerging as important reactive intermediates with interesting structures.\textsuperscript{1} Due to their relatively weak B–H bonds,\textsuperscript{2} NHC-boranes participate as both reagents and reactants in various radical-mediated transformations including photopolymerizations.\textsuperscript{3}

Structural knowledge about NHC-boryl radicals bearing assorted substituents on both the NHC ring and the boron atom comes from direct observation by EPR (Electron Paramagnetic Resonance; also known as Electron Spin Resonance) spectroscopy, often complemented by Density Functional Theory (DFT) calculations.\textsuperscript{4} NHC-boryl radicals are typically planar with spin density delocalized into the NHC ring due to conjugation (Figure 1a). Still, they are best considered as conjugated boryl radicals with carbon atoms in the $\pi$-system (as opposed to conjugated carbon radicals with a boron atom in the $\pi$-system) because they have relatively high spin density on boron and they typically react on boron.\textsuperscript{3,4}

Recently, we tried to make and observe boraallyl radicals \textbf{2} from NHC-alkenyl boranes \textbf{1} bearing two methyl ester substituents (Figure 1b).\textsuperscript{5} However, EPR experiments with \textbf{1} and di-tert-butyl peroxide (DTBP) provided spectra of a single species that did not match expectations for \textbf{2}. Instead, the observed spectra were assigned with the aid of DFT calculations to novel ring-closed 1,2-oxaborole radicals \textbf{3}.

In complementary preparative experiments, reactions of \textbf{1} with AIBN and Bu$_3$SnH provided novel boralactones \textbf{4} as stable products in good yields. These boralactones are oxidized products, and oxygen (from air) is needed for their formation. Based on these results, we concluded that boraallyl radicals \textbf{2} were indeed generated under both EPR and preparative conditions, but they could not be observed by EPR because their 5-\textit{endo} cyclizations to 1,2-
oxaborole radicals 3 were so fast. This conclusion was supported by DFT calculations, which showed that the 5-endo cyclization of 2 to 3 is both exothermic and has a low activation barrier.\(^5\)

(a) Generation and generic structure of NHC-boryl radicals

(b) Unusual 5-endo cyclizations of boraallyl radicals with methyl esters (ref. 5)

(c) EPR observation of two oxaborole radical species with tert-butyl esters (this work)

Figure 1. Structures and reactions of NHC-boryl radicals

As an extension of these studies, we decided to generate radicals from a set of analogous NHC-boranes 5 with di-tert-butyl ester groups (Figure 1c). This was conceived as a worthwhile if relatively routine extension of scope of the new cyclization to form oxaborole radicals. However, the EPR experiments held a surprise in store; we expected to observe one oxaborole radical species 6 on reactions of 5 with DTBP, but instead we observed two. Here we describe
these EPR experiments and associated DFT calculations and assign the two species as non-interconverting (on the EPR timescale at up to 300 K) rotamers of two oxaborole radicals. We also describe improved conditions based on thiol catalysis for preparative conversion of the various di-tert-butyl esters 6 to stable boralactones.

RESULTS AND DISCUSSION

Precursor Synthesis: The alkenylboranes 5a–f used in this study are new compounds that were prepared by reaction of the parent NHC-boranes 8a–f with di-tert-butyl acetylenedicarboxylate 9 (Scheme 1). Under a standard set of conditions, a mixture of the appropriate NHC-borane 8 (1 equiv) and 9 (2 equiv) in THF was refluxed for 12 h. Cooling, solvent removal, and direct purification by automated flash chromatography provided the alkenylborane 5 (less polar) along with the corresponding trans-borirane 10 (more polar). All the alkenyl boranes are pure (E)-isomers that are stable to ambient lab conditions.

Scheme 1. Synthesis of precursor alkenylboranes by hydroboration

Table 1 summarizes the results of these preparative experiments. For the substrates with N,N-dialkyl substituents (entries 1–4 and 6), the ratio of alkenylborane 5 to borirane 10 was about 1/1. Isolated yields of the alkenylboranes 5a–d,f were in the range of 36–44%, while total
isolated yields of both products (5 + 10) ranged from 75–83%. The exception was \( N,N \)-dimesityl substrate, entry 5. This reaction was conducted in acetonitrile, to aid precursor solubility, and provided mostly the borirane 10e (53%) with only 15% of the alkenylborane 5e. The increased amount of borirane in this experiment is due to the N-aryl substituents, not to the solvent change. Because of the small quantities available, 5e was used only for EPR experiments.

### Table 1. Isolated yields of alkenylboranes and boriranes.

<table>
<thead>
<tr>
<th>entry</th>
<th>alkenylborane, yield(^a)</th>
<th>borirane, yield(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5a, 44% ( R^1 = R^2 = \text{Me} )</td>
<td>10a, 32%</td>
</tr>
<tr>
<td>2</td>
<td>5b, 42% ( R^1 = \text{Bu}, R^2 = \text{Me} )</td>
<td>10b, 41%</td>
</tr>
<tr>
<td>3</td>
<td>5c, 39% ( R^1 = \text{Bn}, R^2 = \text{Me} )</td>
<td>10c, 36%</td>
</tr>
<tr>
<td>4</td>
<td>5d, 40% ( R^1 = R^2 = \text{iPr} )</td>
<td>10d, 37%</td>
</tr>
<tr>
<td>5(^b)</td>
<td>5e, 15% ( R^1 = R^2 = \text{Mes} )</td>
<td>10e, 53%</td>
</tr>
<tr>
<td>6</td>
<td>5f, 36%</td>
<td>10f, 40%</td>
</tr>
</tbody>
</table>

\(^{a}\)isolated yield; \(^{b}\)CH\(_3\)CN as solvent

**EPR Spectroscopic Experiments:** Solutions of each of the symmetrical NHC-alkenylboranes 5a, 5d, 5e and 5f, with added DTBP, were prepared in \( \text{tert-} \)-butylbenzene solvent. Each solution was sonicated, then aliquots (0.2 mL) in quartz tubes were deaerated by bubbling \( \text{N}_2 \) and irradiated in the resonant cavity of the 9.5 GHz CW-EPR spectrometer with unfiltered UV light from a 500 W high pressure mercury arc lamp. Initially spectra were run at intervals in the temperature range 220 to 280 K with best results at about 260 K, except for 5e for which the best quality signal was obtained at 220 K.
A spectrum with remarkable resolution was obtained in 2nd derivative mode from precursor alkenylborane 5a at 270 K [see Figure 2(a)]. The spectrum of the major radical present consisted of a set of 8 doublets and was readily simulated with hyperfine splittings (hfs) of $a(1\text{H}) = 25.16$, $a(^{11}\text{B}) = 6.47$ and $a(1\text{H}) = 1.30$ G [see red spectrum (b) in Figure 2]. These hfs were of similar magnitude, where applicable, to those of the ring-closed oxaborole radical 3a previously observed from the analogous precursor containing methyl ester substituents [$a(1\text{H}) = 26.01$, $a(^{11}\text{B}) = 6.01$, $a(1\text{H}) = 1.64$, $a(3\text{H}) = 1.12$ G].6 Hence the main species observed was the ring closed oxaborole radical 6a. The simulation of the same radical with its $^{10}$B-isotope [Figure 2, green trace (c)] also conformed well with this conclusion.

**Figure 2.** Experimental and simulated 2nd derivative CW EPR spectra obtained for ring-closed oxaborole radical 6a from precursor 5a. (a) Experimental spectrum at 270 K; (b) Simulation of major oxaborole rotamer of 6a with $^{11}$B isotope; (c) Simulation of major oxaborole rotamer of 6a
with $^{10}\text{B}$ isotope; (d) Simulation of minor oxaborole rotamer of 6a with $^{11}\text{B}$ isotope; (e) Sum (b + c + d) of simulations.

Surprisingly, the spectrum contained another minor radical (relative concentration 16%) with additional resonance lines most easily observed “outside”, that is to high and low field, of the main doublets. This spectrum was also effectively simulated as another set of 8 doublets [see blue trace (d) in Figure 2; the correlation coefficient for the sum of the simulations was $R = 0.983$]. The g-factor (2.0034) was essentially identical to that of the main species and the hfs $[a(1\text{H}) = 26.17, a^{(1}\text{B}) = 6.58, a(1\text{H}) = 1.38 \text{ G}]$ were so similar as to suggest the major and minor species were structural varieties of the same ring-closed oxaborole radical 6a.

The structural possibilities for oxaborole radical 6a were investigated by means of DFT computations with the B3LYP functional and the 6-311+G(2d,p) basis set. In the lowest energy structure 6aT (Scheme 2 and Figure 4) the C=O group was trans to the partial C=C double bond of the oxaborole ring and pointed approximately towards the NHC ring. Furthermore, the 5-member oxaborole ring, the ester CO$_2$ group and the O-atom of the lactone O'Bu group lay almost in a plane. The comparatively short bond from the ring C-atom to the ester carbonyl-C-atom [rC$_2$–C$^3$] in Scheme 2] i.e. 1.428 Å suggested some double bond character with consequent restricted rotation. The potential energy function for internal rotation of the CO$_2$'Bu group was obtained by successive incrementation of the dihedral angle 4-3-2-1 (see Scheme 2). Similarly, the rotational potential energy function for internal rotation of the O'Bu group (structures 6aP, 6aQ; dihedral angle 7-6-5-4) was also obtained and these energy profiles are illustrated in Figure 3.
Scheme 2. Conformational interconversions of 1,2-oxaborole radicals 6a. Top: CO$_2$Bu rotor; bottom: O'Bu rotor.

Figure 3. DFT potential energy functions for internal rotations in 1,2-oxaborole radicals 6a and related species. Blue curve: torsional rotation of the CO$_2$Bu group (dihedral angle 4-3-2-1) in 6a. Red curve: torsional rotation of the CO$_2$Me group in 3a. Black curve: rotation of the O'Bu group in 6a (dihedral 4-5-6-7). Purple curve: torsional rotation of the CO$_2$Bu group in boralactone 7a.
The black curve (Figure 3) for torsion of the O' Bu group indicated only one stable conformation. Furthermore, the comparatively low computed energy barrier (~ 5 kcal/mol) suggested this motion would not be observable by EPR spectroscopy in the accessible temperature range. That is, the spectrum would be an average over all rotational states. On the other hand, the potential energy function for rotation of the CO₂' Bu group was approximately that of a twofold rotor with just two stable rotamers (blue curve in Figure 3). The lowest energy rotamer, labelled 6aT in Scheme 2 and Figure 4, had a dihedral angle 4-3-2-1 close to 0° such that the C=O of the ester group was trans to the adjacent ring C=C double bond and pointed towards the NHC ring. The second rotamer, labelled 6aC in Scheme 2 and Figure 4, with its C=O group cis to the adjacent ring C=C double bond and pointing away from the NHC ring, had dihedral angle 4-3-2-1 close to 180° and was only 2.6 kcal/mol higher in energy.

Figure 4. (a) DFT computed structures of internal rotation of the CO₂' Bu group of oxaborole radical 6a. Left; rotamer 6aT, center; TS, right; rotamer 6aC; (b) SOMO for 6aT; (c) SOMO for 6aC.
The HOMOs for the two stable rotamers are also illustrated in Figure 4. Interestingly, the HOMO for 6aT consisted of an extensive $\pi$-system spanning the whole planar portion of the molecule including the ester C=O group (Figure 4 (b)). The second stable rotamer 6aC contained an analogous planar region also covered by an extended $\pi$-system (Figure 4 (c)). The resonance electron delocalization resulting from these $\pi$-systems partly explains why these particular rotamers are energy minima. The comparatively high computed torsion barriers (15.4 and 14.8 kcal/mol) implied that interconversion of 6aT and 6aC would be very slow in the accessible temperature range. Consequently, these two rotamers should appear as separate species in the EPR spectrum. This DFT data enabled us to identify with some confidence 6aT as the major radical present in the EPR spectrum and 6aC as the minor radical.

Another conclusion from the DFT data is that CO$_2$tBu groups in oxaborole radicals analogous to 6a, but having different substituents on their NHC rings, should also have twofold torsional rotors. As predicted, the EPR spectra obtained from UV irradiation of solutions of 5d, 5e and 5f each with DTBP did indeed demonstrate the presence of two rotamers of the corresponding oxaborole radicals. The spectra of 6d-f were not so well resolved as in the case of radical 6a but good simulations were achieved on inclusion of the second species. Sample spectra are included in the Supporting Information and the derived EPR parameters are in Table 2. The EPR results afforded good evidence that H-abstraction took place readily from precursors 5 and that the resulting boraallyl radicals (analogous to 2 but with 'Bu esters) ring closed very rapidly, even at 220 K, in 5-endo-mode onto the O-atoms of the ester substituents.
Table 2. Experimental and computed EPR parameters for 1,2-oxaborole radicals 6 and 3.

<table>
<thead>
<tr>
<th>Radical</th>
<th>T/K or DFT$^b$</th>
<th>Rel. $^a$</th>
<th>$g$-factor</th>
<th>$a(11\text{B})$</th>
<th>$a(10\text{B})$</th>
<th>$a(\text{H}^\text{B})$</th>
<th>$a(\text{H}^\text{A})$</th>
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<td>1.18(3H)</td>
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$^a$ Hfs in Gauss (G); note that EPR provides only the magnitude not the sign of hfs. $^b$ DFT at the UB3LYP/6-311+G(2d,p) level of theory on oxaboroles with dimethyl-NHC units. $^c$ Correlation coefficients of the computer simulations. $^d$ UB3LYP/epr-iii//UB3LYP/6-311+G(2d,p).
The spectra from radicals $6a_T$ and $6a_C$ were examined in the temperature range 220 to 280 K and showed the two distinct rotamers throughout. The ratio $6a_T/6a_C$ was 84/16 at 270 K. It follows that interconversion of rotamer $6a_T$ with $6a_C$ was too slow for observation by EPR. Likewise, the spectra of radicals $6e$–$f$ all showed two rotamers with $T/C$ ratios of about 80/20. It is probable, therefore, that all the mixtures $6T$ and $6C$ were formed by hydrogen abstraction from corresponding conformations of the of the $E$-alkenylboranes $5$. In essence then, we can infer the rotamer ratios of precursors $5$ (roughly 4/1 favoring $s$-$trans$) even though the rotation barriers in $5$ are too low for direct measurement (for example, NMR spectra of $5$ exhibit only a single set of signals). The assumption in this inference is that $tert$-butoxy radicals react with the two rotamers of $5$ at about the same rate.

The EPR spectra from all four precursors recorded at temperatures above about 300 K became more complex showing the presence of several radicals that could not be identified. These EPR spectra afforded no evidence of the formation of $tert$-butyl radicals from $\beta$-scission of 1,2-oxaborole radicals $6$. EPR spectra were also run on solutions of $5f$ containing AIBN (2,2'-azobis(2-methylpropionitrile)) in place of DTBP. In the absence of UV irradiation, no EPR signals were detected at temperatures up to 350 K. When UV irradiation was introduced, the spectrum of the initiator-derived 2-cyanoprop-2-yl radical appeared. Prolonged heating with AIBN led to complex spectra but again no evidence for formation of $tert$-butyl radicals was obtained.

The two distinguishable rotamers of the set of ring-closed oxaborole radicals $6T$ and $6C$ resemble the $s$-$trans$ and $s$-$cis$ rotamers of $\alpha,\beta$-unsaturated carbonyl compounds (Scheme 2, $11T$ and $11C$), except that the ring C–C bonds of oxaborole radicals $6T$ and $6C$ have only partial double bond character. The barrier to internal rotation in acrolein ($11$, $X = \text{H}$) is only about 5
kcal/mol, as judged by ultrasonic\textsuperscript{7} and microwave spectroscopy measurements.\textsuperscript{8} Similarly, the barrier in acrylic acid (11, X = OH) was found experimentally to be 3.8 kcal/mol.\textsuperscript{9} Accordingly, conjugation of a carbonyl group with a C=C double bond creates a rotation barrier around a connecting single C–C bond of about 4–5 kcal/mol. However, the rotation barrier computed for oxaborole radicals 6aT and 6aC was calculated to be much higher at 14.6 kcal/mol, and a comparatively high value was supported by the EPR observation of distinct species. It follows that some other factor(s) must come into play.

For $\alpha$-(alkoxycarbonyl)alkyl radicals 12T and 12C (X = OR) [and related species (X = alkyl, NR\textsubscript{2})] Fischer and co-workers observed two distinct rotamers by EPR spectroscopy.\textsuperscript{10} and also by muon spin resonance.\textsuperscript{11} Newcomb and co-workers also adduced evidence for two conformational isomers for related ester radicals and showed that they reacted at different rates.\textsuperscript{12} Furthermore, the energy barriers to internal rotation of these $\alpha$-carbonylalkyl radicals were all determined to be in the range 10–12 kcal/mol.\textsuperscript{10-12}

These structures and barrier heights show 12T and 12C to be better models for the oxaborole radicals. The comparatively large energy barriers to internal rotation, about what are formally single bonds in radicals 6, can therefore be attributed to partial $\pi$-electron delocalization. The •C–C=O units in oxaborole radicals 6 are partly allylic in character. More accurately the delocalization is quasi-pentadienylic because of the additional adjacent double bond in the oxaborole ring. The analogous internal rotation barrier •C–C=C in the archetype allyl radical is somewhat higher at 15.7 kcal/mol\textsuperscript{13} as expected for full allylic character. The ratio of the s-\textit{trans}-6 to s-\textit{cis}-6 rotamers is close to 4:1 irrespective of the $N,N$-substituents on the NHC ring (see Table 2). Thus, steric hindrance from these substituents does not change the
rotamer populations and probably does not contribute much to the height of the ester internal rotation barriers either.

The torsion of the CO$_2$Bu group in the isolated product boralactone 7a was also examined by DFT computation. The potential energy function (purple curve in Figure 3) was similar in shape to that of the oxaborole radical showing an approximate twofold rotor with two stable conformations having their C=O groups s-trans and s-cis to the ring double bond and differing in energy by 3.2 kcal/mol. The computed barrier heights (4.7 and 5.4 kcal/mol) were considerably lower than for the oxaborole radicals because of the absence of the allylic type stabilization of the unpaired electron. As expected, these rotamers resemble those of $\alpha,\beta$-unsaturated carboxyls 11T and 11C.

If these conclusions are correct, then it follows that distinct s-trans and s-cis rotamers would be expected for the analogous methyl ester containing oxaborole radicals 3 even though these were not detected in the original study. Internal rotation of the CO$_2$Me group in the dimethyl-NHC-oxaborole radical 3a was therefore also examined by DFT computation. The computed potential energy function (red curve in Figure 3) revealed a twofold rotor very similar to that for analogous rotation of the CO$_2$Bu group. Two stable rotamers 3aT and 3aC were indicated with their C=O groups in virtually the same orientations as in the CO$_2$Bu analogs and differing in energy by only 2.4 kcal/mol. The rotational energy barriers (15.8 and 15.0 kcal/mol) were also similar and lent support to the idea that distinct rotamers should be observable for these species.

The previous EPR spectra of methyl ester containing oxaborole radicals 3 are considerably more complex than the new spectra of 6 because couplings to the methyl H-atoms of both the MeCO$_2$ and the MeO substituents are fully or partially resolved. These 1$^{st}$
derivative EPR spectra gave no ostensible evidence for the presence of two rotamers. However, due to the intricate patterns of complex multiplets, minor proportions of a second rotamer could have gone undetected.

To look for the minor rotamer, a well resolved 2\textsuperscript{nd} derivative spectrum for a methyl ester oxaborole radical 3 was needed (see Scheme 3). EPR spectra of the \(N,N\)-dimethyl-NHC-oxaborole radical 3a were too weak and short-lived at all temperatures to permit recording in 2\textsuperscript{nd} derivative mode. It is likely that the complexity and greater natural linewidth of the EPR spectrum of the \(N,N\)-di-dipp-NHC-oxaborole 3g would obscure any minor rotamer even in a 2\textsuperscript{nd} derivative spectrum.


We were, however, able to obtain a spectrum of the \(N,N\)-di-\textsuperscript{i}Pr-NHC-oxaborole 3d in 2\textsuperscript{nd} derivative mode in a mixed solvent (Figure 5(a)).\textsuperscript{14} This spectrum revealed some asymmetry, and additional resonance lines were resolved. The simulation with just one rotamer of the methyl ester group (Figure 5(b)) had a correlation coefficient of 0.867, but a much-improved fit (R = 0.971) was achieved by inclusion of 19\% of a second conformation (Figure 5(c)). The spectral asymmetry was attributable to a very slight difference in the \(g\)-factors of the two rotamers. See Table 2 for the resultant EPR parameters.
Figure 5. Experimental and simulated 2nd derivative CW EPR spectra obtained for ring-closed oxaborole radical 3d from precursor 1d. (a) Black: experimental spectrum at 260 K in Ph'Bu containing 5% allyl bromide. (b) Red: simulation of major oxaborole rotamer of 3dT with $^{11}$B and $^{10}$B isotopes. (c) Blue: simulation including major (3dT) and minor (3dC) rotamers of oxaborole radicals.

The detection of two rotamers of radical 3d supports the idea that the internal rotation barriers arise from delocalization of the unpaired electron in the quasi-pentadieneylic $\pi$-systems. We conclude that two stable rotamers exist for RCO$_2$ substituents in other NHC-oxaborole radicals 3, even though their signals cannot be resolved in their EPR spectra.

Preparative Reactions: To make boralactones, we initially used the conditions developed for the corresponding dimethyl esters as shown in Figure 6a. In this earlier work, alkenylboranes 1
were heated in benzene (80˚ C, 6 h) with AIBN (50 mol%) and Bu$_3$SnH (50 mol%) to provide NHC-boralactones 4 in isolated yields of about 60%. This procedure requires dioxygen for product formation, and preparative reactions are prone to stopping if the source is ambient air.

This published procedure worked reasonably well for the di-tert-butyl esters. For example, reaction of 5a (R$^1$ = R$^2$ = Me) under these conditions provided 7a in 44% yield according to $^{11}$B NMR analysis of the crude product. However, substituting tert-dodecanethiol for tin hydride (Figure 6b) proved to be more practical because the products are free from tin.$^{15}$ For example, reaction of 5a under the thiol conductions provided 7a in 70% yield according to $^{11}$B NMR analysis. A control experiment quickly showed that this procedure does not require dioxygen, so the subsequent experiments were conducted under argon to discourage oxidation of the thiol to a disulfide.

Figure 6. Conditions for boralactone formation

The structures and yields of the boralactones made by this procedure are shown in Figure 7. According to $^{11}$B NMR analysis, the boralactones 7a–d were formed in 64–70% yields. All
these boralactones are polar and purification by flash chromatography gave mixed results.

Boralactones 7b, 7d and 7f were isolated in good purity yields of 56%, 54% and 50%, respectively. Boralactone 7c was isolated in 57% yield and was about 90% pure, while 7a was isolated in 59% yield and was about 72% pure. The purities were determined by $^{11}$B NMR spectroscopy, where the impurities show a very broad signal at about 0–5 ppm. This signal, which was present in the spectra of all the crude products, was completely removed for 7b, 7d and 7f, partially removed for 7a, and not removed for 7c.

**Figure 7.** Structures and $^{11}$B NMR yields of new boralactones (isolated yields are in parentheses).

**Reaction Mechanism:** Figure 8 shows a thiol-catalysis mechanism for boralactone formation that is consistent with the experimental results. Starting from boraalkeny radical 11, rapid ($k$ probably $> 10^8$ s$^{-1}$) 5-endo cyclization provides oxaborole radical 6. This undergoes $\beta$-fragmentation to provide boralactone 7 and tert-butyl radical. This $\beta$-fragmentation does not occur when methyl is the departing radical, and even the liberation of the tert-butyl radical must be relatively slow ($k$ probably $< 10^5$ s$^{-1}$) because it is not observed by EPR spectroscopy (see
above). Based on prior work on thiol catalysis of NHC-borane reactions,\textsuperscript{3g,16} we suggest that the \textit{tert}-butyl radical abstracts hydrogen from \textit{tert}-dodecanethiol to give the corresponding thiy radical and \textit{tert}-butane. In turn, the thiy radical abstracts hydrogen from the starting alkenylborane 5 to give back the thiol and the starting alkenylboryl radical 11, thereby closing the chain cycle. This is a net redox-neutral reaction in which one product (the boralactone 7) is oxidized relative to that starting alkenylborane 5 and the other (\textit{tert}-butane) is reduced.

![Putative thiol-catalysis mechanism for boralactone formation](image)

**Figure 8.** Putative thiol-catalysis mechanism for boralactone formation

To support the thiol catalysis mechanism, we conducted an experiment with 5d under the standard conditions but reducing the amount of thiol from 50 mol\% to 20 mol\%. This provided 7d in 68\% NMR yield and 53\% isolated yield (compare this to Figure 8, 64\% NMR yield and 54\% isolated yield of 7d with 50 mol\% thiol). Thus, a decrease in thiol amount by a factor of 2.5 does not materially affect the outcome of the reaction.

Support for the fragmentation of oxaborole radical 6a to boralactone 7a and \textit{tert}-butyl radical was obtained from DFT computations. The transition state (TS) for extrusion of \textit{tert-
butyl radical from 6a was located, and the resulting overall energetics and activation parameters are compared with those obtained previously\(^6\) for methyl radical extrusion from 3a in Scheme 4 (see Supporting Information for details).

**Scheme 4.** DFT study of 1,2-oxaborole radical fragmentation. Method: B3LYP/6-311+G(2d,p); energies in kcal/mol

![Scheme 4](image)

The fragmentation of 3a was computed to be endothermic and both the activation enthalpy (\(\Delta H^\ddagger = 22.0\) kcal mol\(^{-1}\)) and activation free energy (\(\Delta G^\ddagger = 21.0\) kcal mol\(^{-1}\)) were too high for the elimination of methyl radical to be viable in solution. However, the fragmentation of 6a to form tert-butyl radical was computed to be marginally exothermic (\(\Delta H^0 = -1.2\) kcal/mol) and strongly exoergic (\(\Delta G^0 = -15.2\) kcal/mol). Furthermore, both the activation enthalpy and free energy for loss of tert-butyl radical were low enough for the process to be viable at 80° C in solution (\(\Delta H^\ddagger = 12.1\) kcal/mol; \(\Delta G^\ddagger = 15.0\) kcal/mol). These DFT results support the mechanism proposed in Figure 8.

**CONCLUSIONS**
The straightforward hydroboration procedure with various NHC-BH$_3$ reagents succeeded as well with di-tert-butyl acetylenedicarboxylate as with the dimethyl-analogs. Most of the NHC-BH$_3$ reagents afforded readily separable mixtures of alkenyl NHC-boranes and boriranes in a ratio of about 1:1.

Hydrogen atom abstraction from tert-butyl ester-substituted NHC-alkenyl boranes by tert-butoxyl radicals was fast, generating boraallyl radicals 8. The latter were not detectable by EPR spectroscopy even at 220 K but rapidly underwent an unusual 5-endo ring closure onto the O-atom of the distal tert-butyl ester group. The EPR spectra showed the cyclization step to be fast at 220 K; as had previously been found for closure onto a methyl ester group. The allylic stabilization and extended π-conjugation of the oxaborole radicals undoubtedly contributed to the ease of these ring closure steps. Two distinct rotamers of each oxaborole radical were characterized by EPR spectroscopy and DFT computations. In these s-trans (6T) and s-cis (6C) rotamers the ester C=O groups adopted trans and cis orientations relative to the oxaborole ring C=C double bonds. The stability of these structures was due to the quasi-allylic interaction of the unpaired electron with the ester C=O group.

These observations implied that two stable rotamers of the analogous methyl ester substituted oxaborole radicals should also exist. Indeed, for one MeCO$_2$-containing oxaborole radical with a di-isopropyl-NHC unit, two distinct rotamers were spectroscopically characterized. It is likely that other MeCO$_2$-containing oxaborole radicals also exist as pairs of rotamers, but their EPR spectra are too complex for these to be distinguished with this spectroscopic technique. Newcomb and co-workers showed that the two analogous rotamers of appropriately unsaturated α-(alkoxycarbonyl)alkyl radicals reacted at different rates in subsequent cyclization steps.\textsuperscript{12} It is therefore likely that the two rotamers of oxaborole radicals have different
reactivities particularly at C-3 (see Scheme 2). However, in our preparative processes (Figure 6) reaction took place at C-5 which is comparatively remote from the ester group. Differential reactivity at C-5 of the two ester conformations of oxaborole radicals will probably be insignificant.

The new preparative protocol for the boralactones, involving tert-dodecanethiol avoids the use of the neurotoxic tin hydride while also affording very acceptable yields. The products are examples of the rare NHC complexes of borinic acid lactones. They were found to be robust molecules with long shelf lives.

EXPERIMENTAL SECTION

Synthesis and Characterization of (E)-alkenyloboranes and Boriranes

Di-tert-butyl but-2-ynedioate (di-tert-butyl acetylenedicarboxylate): tert-Butyl acetate (23.2 g, 200 mmol) and triflic acid (0.60 g, 4 mmol) were added dropwise to a solution of acetylenedicarboxylic acid (2.28 g, 20 mmol) in 150 mL of DCM at 0 °C. The resulting solution was warmed to room temperature with stirring for 2 h before saturated NaHCO₃ was slowly introduced. The aqueous layer was extracted with DCM (4 x 100 mL). The combined organic layer was washed with saturated NaCl, then dried over MgSO₄, filtered, and concentrated under reduced pressure to give crude product. This was purified by flash chromatography on silica (hexane:ethyl acetate) to afford the diester (3.16 g, 70%) as a colorless solid.

General hydroboration procedure: The NHC-borane (1 mmol) was added to a flask containing THF (10 mL), then di-tert-butyl acetylenedicarboxylate (0.45 g, 2 mmol) was added dropwise. The reaction mixture was heated at reflux. After 12 h, the mixture was concentrated,
and the resulting residue was purified by flash chromatography (hexane:ethyl acetate) to afford 
(E)-alkenylborane (less polar) followed by borirane (more polar).

(E)-(1,4-Di-tert-butoxy-1,4-dioxobut-2-en-2-yl)(1,3-dimethyl-1H-imidazol-3-ium-2-
yl)dihydroborate (5a) and 2,3-bis(tert-butoxycarbonyl)-1-(1,3-dimethyl-1H-imidazol-3-ium-
2-yl)boriran-1-uide (10a): This experiment was conducted with 8a (110 mg) and provided 5a 
(148 mg, 44%, white solid, mp 79–81 °C) and 10a (108 mg, 32%, yellow solid, mp 52–53 °C) 
after purification.

5a: $^1$H NMR (500 MHz, CDCl$_3$) δ 6.77 (s, 2H), 6.23 (s, 1H), 3.70 (s, 6H), 1.39 (s, 9H), 1.33 (s, 
9H); $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) δ 174.7, 167.9, 127.6, 120.1, 79.3, 79.2, 36.1, 28.2, 28.1; 
$^{11}$B NMR (160 MHz, CDCl$_3$) δ –28.8 (t, $J = 88$ Hz); HRMS (ESI, TOF) m/z [M – H]$^+$ calculated 
for C$_{17}$H$_{28}$BN$_2$O$_4$ 335.2142, found 335.2164.

10a: $^1$H NMR (500 MHz, CDCl$_3$) δ 6.84 (s, 2H), 3.77 (s, 6H), 1.99 (dd, $J = 8.1$, 5.5 Hz, 1H), 
1.82 (t, $J = 4.8$ Hz, 1H), 1.37 (s, 9H), 1.17 (s, 9H); $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) δ 177.2, 
176.9, 120.7, 77.4, 77.1, 36.0, 28.5, 28.2; $^{11}$B NMR (160 MHz, CDCl$_3$) δ –27.0 (d, $J = 123$ Hz); 
HRMS (ESI, TOF) m/z [M + H]$^+$ calculated for C$_{17}$H$_{30}$BN$_2$O$_4$ 337.2299, found 337.2321.

(E)-(3-Butyl-1-methyl-1H-imidazol-3-ium-2-yl)(1,4-di-tert-butoxy-1,4-dioxobut-2-en-2-
yl)dihydroborate (5b) and 2,3-bis(tert-butoxycarbonyl)-1-(3-butyl-1-methyl-1H-imidazol-3-
im-2-yl)boriran-1-uide (10b): This experiment was conducted with 8b (152 mg) and provided 
5b (160 mg, 42%, colorless oil) and 10b (157 mg, 41%, colorless oil) after purification.

5b: $^1$H NMR (500 MHz, CDCl$_3$) δ 6.80 (d, $J = 1.9$ Hz, 1H), 6.78 (d, $J = 1.9$ Hz, 1H), 6.26 (s, 
1H), 4.13–4.04 (m, 2H), 3.73 (s, 3H), 1.71 (m, 2H), 1.42 (s, 9H), 1.35 (s, 9H), 0.92 (t, $J = 7.4$ 
Hz, 3H); $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) δ 174.6, 167.9, 127.7, 120.2, 118.5, 79.2, 79.1, 48.5,
36.1, 32.4, 28.2, 28.1, 19.8; 11B NMR (160 MHz, CDCl₃) δ –28.8 (t, J = 88 Hz); HRMS (ESI, TOF) m/z [M – H]⁺ calculated for C₂₀H₃₄BN₂O₄ 377.2612, found 377.2628.

10b: ¹H NMR (500 MHz, CDCl₃) δ 6.84 (d, J = 8.2 Hz, 2H), 4.22 (m, 2H), 3.83 (s, 3H), 2.06 (dd, J = 8.2, 5.5 Hz, 1H), 1.86 (t, J = 4.9 Hz, 1H), 1.81 (m, 2H), 1.43 (s, 9H), 1.24 (s, 9H), 0.97 (t, J = 7.4 Hz, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 177.3, 177.1, 120.5, 119.3, 77.5, 77.2, 48.8, 36.1, 32.3, 28.5, 28.3, 19.7, 13.6; ¹¹B NMR (160 MHz, CDCl₃) δ –26.9 (d, J = 123 Hz); HRMS (ESI, TOF) m/z [M + H]⁺ calculated for C₂₀H₃₆BN₂O₄ 379.2768, found 379.2786.

(\(E\))-\((3\)-Benzyl-\(1\)-methyl-\(1\H\)-imidazol-3-ium-2-yl)\((1\)-di-\(\text{tert}\)-butoxy-\(1\H\)-dioxobut-2-en-2-yl)dihydroborate (5c) and 1-(\(3\)-benzyl-\(1\)-methyl-\(1\H\)-imidazol-3-ium-2-yl)-2,3-bis(\(\text{tert}\)-butoxycarbonyl)boriran-1-uide (10c): This experiment was conducted with 8c (186 mg) and provided 5c (161 mg, 39%, yellow solid) and 10c (148 mg, 36%, yellow solid, mp 66–68 °C) after purification.

5c: ¹H NMR (500 MHz, CDCl₃) δ 7.27–7.19 (m, 5H), 6.69 (d, J = 2.0 Hz, 1H), 6.56 (d, J = 2.0 Hz, 1H), 6.22 (s, 1H), 5.27 (s, 2H), 3.72 (s, 3H), 1.34 (s, 9H), 1.32 (s, 9H); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 167.9, 135.9, 128.8, 128.6, 128.2, 127.9, 120.5, 118.5, 79.3, 77.2, 52.2, 36.2, 28.2, 28.1; ¹¹B NMR (160 MHz, CD₃CN) δ –28.6 (t, J = 88 Hz); HRMS (ESI, TOF) m/z [M – H]⁺ calculated for C₂₃H₃₂BN₂O₄ 411.2455, found 411.2473.

10c: ¹H NMR (500 MHz, CDCl₃) δ 7.35 (s, 5H), 6.82 (d, J = 2.0 Hz, 1H), 6.76 (d, J = 1.9 Hz, 1H), 5.46 (d, J = 14.7 Hz, 1H), 5.36 (d, J = 14.7 Hz, 1H), 3.86 (s, 3H), 2.13 (dd, J = 8.1, 5.5 Hz, 1H), 1.94 (t, J = 4.9 Hz, 1H), 1.42 (s, 9H), 1.29 (s, 9H); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 177.2, 129.0, 128.6, 128.6, 120.9, 119.2, 77.6, 77.4, 52.5, 36.2, 28.5, 28.3, 28.2; ¹¹B NMR (160 MHz, CDCl₃) δ –26.9 (d, J = 123 Hz); HRMS (ESI, TOF) m/z [M + H]⁺ calculated for C₂₃H₃₄BN₂O₄ 413.2629, found 413.2629.
(E)-(1,4-Di-tert-butoxy-1,4-dioxobut-2-en-2-yl)(1,3-diisopropyl-1H-imidazol-3-ium-2-yl)dihydroborate (5d) and 2,3-bis(tert-butoxycarbonyl)-1-(1,3-diisopropyl-1H-imidazol-3-ium-2-yl)boriran-1-uide (10d): This experiment was conducted with 8d (166 mg) and provided 5d (157 mg, 40%, white solid, mp 98–100 °C) and 10d (145 mg, 37%, white solid, mp 103–105 °C) after purification.

5d: $^1$H NMR (500 MHz, CDCl$_3$) δ 6.91 (s, 2H), 6.18 (s, 1H), 5.15 (hept, $J = 6.8$ Hz, 2H), 1.40 (s, 9H), 1.39 (s, 9H), 1.37 (s, 6H), 1.36 (s, 6H); $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$) δ 174.8, 167.6, 126.4, 115.0, 79.0, 49.2, 28.2, 28.2, 22.9; $^{11}$B NMR (160 MHz, CDCl$_3$) δ –28.8 (t, $J = 88$ Hz); HRMS (ESI, TOF) $m/z$ [M – H]$^+$ calculated for C$_{21}$H$_{36}$BN$_2$O$_4$ 391.2768, found 391.2787.

10d: $^1$H NMR (500 MHz, CDCl$_3$) δ 6.96 (s, 2H), 5.33–5.19 (m, 2H), 2.02 (dd, $J = 7.9$, 5.4 Hz, 1H), 1.86 (t, $J = 5.0$ Hz, 1H), 1.43 (m, 21H), 1.31–1.23 (m, 9H); $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$) δ 177.5, 177.3, 115.7, 115.6, 77.4, 49.8, 28.6, 28.5, 28.0, 23.3, 22.8; $^{11}$B NMR (160 MHz, CDCl$_3$) δ –26.9 (d, $J = 121$ Hz); HRMS (ESI, TOF) $m/z$ [M + H]$^+$ calculated for C$_{21}$H$_{38}$BN$_2$O$_4$ 393.2925, found 393.2942.

(E)-(1,4-Di-tert-butoxy-1,4-dioxobut-2-en-2-yl)(1,3-dimesityl-1H-imidazol-3-ium-2-yl)dihydroborate (5e) and 2,3-bis(tert-butoxycarbonyl)-1-(1,3-dimesityl-1H-imidazol-3-ium-2-yl)boriran-1-uide (10e): This experiment was conducted with 8e (318 mg) and provided 5e (82 mg, 15%, white solid) and 10e (289 mg, 53%, white solid) after purification.

5e: $^1$H NMR (500 MHz, CDCl$_3$) δ 6.91 (s, 4H), 6.89 (s, 2H), 6.07 (s, 1H), 2.31 (s, 6H), 2.15 (s, 12H), 1.37 (s, 9H), 1.30 (s, 9H); $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$) δ 172.3, 138.6, 135.5, 134.4, 130.9, 120.0, 120.8, 78.4, 78.1, 77.2, 28.3, 28.1, 21.1, 18.1; $^{11}$B NMR (160 MHz, CDCl$_3$) δ –28.3 (t, $J = 91$ Hz); HRMS (ESI, TOF) $m/z$ [M – H]$^+$ calculated for C$_{33}$H$_{44}$BN$_2$O$_4$ 543.3394, found 543.3402.
10e: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.01 (s, 2H), 7.00 (s, 2H), 6.96 (s, 2H), 2.36 (s, 6H), 2.18 (s, 6H), 2.12 (s, 6H), 1.57 (dd, $J = 8.7, 6.5$ Hz, 1H), 1.31 (s, 9H), 1.29 (s, 9H), 1.13–1.08 (m, 1H); $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$) δ 178.2, 176.9, 139.1, 135.1, 135.0, 134.0, 129.5, 129.3, 122.0, 28.6, 28.5, 21.1, 18.3, 18.2; $^{11}$B NMR (160 MHz, CDCl$_3$) δ –26.0 (d, $J = 122$ Hz); HRMS (ESI, TOF) m/z [M + H]$^+$ calculated for C$_{33}$H$_{46}$BN$_2$O$_4$ 545.3550, found 545.3557.

(E)-(1,4-Di-tert-butoxy-1,4-dioxobut-2-en-2-yl)(1,3-dimethyl-1H-benzo[d]imidazol-3-ium-2-yl)dihydroborate (5f) and 2,3-bis(tert-butoxycarbonyl)-1-(1,3-dimethyl-1H-benzo[d]imidazol-3-ium-2-yl)boriran-1-uide (10f): This experiment was conducted with 8f (160 mg) and provided 5f (139 mg, 36%, yellow solid, mp 100–101 °C) and 10f (155 mg, 40%, yellow solid, mp 170–172 °C) after purification.

5f: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.46–7.41 (m, 2H), 7.38 (m, 2H), 6.35 (s, 1H), 3.95 (s, 6H), 1.32 (s, 9H), 1.31 (s, 9H); $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$) δ 174.4, 167.8, 133.2, 128.2, 123.9, 110.7, 79.4, 32.3, 28.1, 28.0; $^{11}$B NMR (160 MHz, CDCl$_3$) δ –28.4 (t, $J = 89$ Hz); HRMS (ESI, TOF) m/z [M – H]$^–$ calculated for C$_{21}$H$_{30}$BN$_2$O$_4$ 385.2299, found 385.2317.

10f: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.50–7.39 (m, 4H), 4.04 (s, 6H), 2.19 (dd, $J = 8.3, 5.4$ Hz, 1H), 1.97 (t, $J = 5.0$ Hz, 1H), 1.46 (s, 9H), 1.11 (s, 9H); $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$) δ 177.0, 176.8, 132.8, 124.8, 121.2, 111.0, 107.3, 77.7, 77.3, 32.5, 28.5, 28.1, 26.0; $^{11}$B NMR (160 MHz, CDCl$_3$) δ –26.9 (d, $J = 123$ Hz); HRMS (ESI, TOF) m/z [M + H]$^+$ calculated for C$_{21}$H$_{32}$BN$_2$O$_4$ 387.2455, found 387.2474.

DFT Calculations

DFT calculations were carried out using the Gaussian 09 suite of programs. Results were obtained with the B3LYP functional and the 6-311+G(2d,p) basis set was employed with the
CPCM continuum model with toluene as solvent. Default values of the keywords Alpha, Radii, TSNUM, and TSARE were employed. Vibrational frequency calculations were implemented so that GS (no imaginary frequencies) and TS status could be checked (one imaginary frequency), and enthalpies and free energies were adjusted for zero point and thermal corrections to 1 atm and 298 K.

**EPR Experiments**

CW-EPR spectra were obtained at 9.5 GHz with 100 kHz modulation employing a commercial spectrometer fitted with a rectangular ER4122 SP resonant cavity. Stock solutions of each sample (2 to 15 mg) and DTBP (1 equiv. wt/wt) in solvent (0.5 mL) were prepared and sonicated if necessary. An aliquot (0.2 mL), to which any additional reactant had been added, was placed in a 4 mm o. d. quartz tube and de-aerated by bubbling nitrogen for 15 min. Photolysis in the resonant cavity was by unfiltered light from a 500 W super pressure mercury arc lamp. In all cases where spectra were obtained, hfs were assigned with the aid of computer simulations using the Bruker SimFonia and NIEHS Winsim2002 software packages. EPR signals were digitally filtered and double integrated using the Bruker WinEPR software. The majority of EPR spectra were recorded with 2.0 mW power, 0.8 G$_{pp}$ modulation intensity and a gain of ca. 10$^6$.

**Synthesis and Characterization of Boralactones**

**General Procedure:** The (E)-alkenyl borane (0.1 mmol), benzene (1 mL), AIBN (8.2 mg, 0.05 mmol) and *terr*-dodecanethiol (10.1 mg, 0.05 mmol) were mixed and placed in a round bottomed flask with stir bar. The mixture was stirred at 80 °C under argon. After 6 h the reaction mixture
was concentrated under reduced pressure. The crude residue was purified by flash chromatography to afford the boralactone.

**3-(**tert-*Butoxycarbonyl)**-2-(3-butyl-1-methyl-1H-imidazol-3-ium-2-yl)-5-oxo-2,5-dihydro-1,2-oxaborol-2-uide (7b):** This experiment was conducted with 5a (37.8 mg) and provided 7b (18.0 mg, 56%, colorless oil) after purification. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.92 (d, $J$ = 7.8 Hz, 2H), 6.61 (d, $J$ = 2.0 Hz, 1H), 4.16 (ddd, $J$ = 13.7, 8.5, 6.8 Hz, 1H), 3.96 (ddd, $J$ = 13.7, 8.4, 6.6 Hz, 1H), 3.73 (s, 3H), 1.79 – 1.69 (m, 2H), 1.41 (s, 9H), 1.38–1.25 (m, 2H), 0.92 (t, $J$ = 7.4 Hz, 3H); $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$ 176.2, 166.5, 132.0, 121.2, 119.4, 79.3, 47.9, 35.2, 31.8, 27.1, 18.7, 12.6; $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ –5.9 (d, $J = 107$ Hz); HRMS (ESI, TOF) $m/z$ [M + H]$^+$ calculated for C$_{16}$H$_{26}$BN$_2$O$_4$ 321.1980, found 321.1999.

**3-(**tert-*Butoxycarbonyl)**-2-(1,3-diisopropyl-1H-imidazol-3-ium-2-yl)-5-oxo-2,5-dihydro-1,2-oxaborol-2-uide (7d):** This experiment was conducted with 5d (39.2 mg) and provided 7d (18.0 mg, 54%, colorless oil) after purification. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.09 (s, 2H), 6.58 (d, $J$ = 2.0 Hz, 1H), 4.87 (hept, $J$ = 6.7 Hz, 2H), 1.44 (d, $J$ = 6.7 Hz, 6H), 1.40 (s, 9H), 1.38 (d, $J$ = 6.7 Hz, 3H); $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$ 177.2, 167.6, 132.0, 121.2, 119.4, 79.3, 49.9, 28.1, 23.4, 23.2; $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ –6.1 (broad); HRMS (ESI, TOF) $m/z$ [M + H]$^+$ calculated for C$_{17}$H$_{28}$BN$_2$O$_4$ 335.2136, found 335.2148.

**3-(**tert-*Butoxycarbonyl)**-2-(1,3-dimethyl-1H-benzo[d]imidazol-3-ium-2-yl)-5-oxo-2,5-dihydro-1,2-oxaborol-2-uide (7f):** This experiment was conducted with 5f (38.6 mg) and provided 7f (16.4 mg, 50%, pale yellow oil) after purification. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.56–7.52 (m, 2H), 7.50 (m, 2H), 6.67 (d, $J$ = 2.1 Hz, 1H), 3.96 (s, 6H), 1.39 (s, 9H); $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) $\delta$ 177.3, 167.3, 133.5, 133.2, 125.3, 111.4, 80.5, 32.3, 28.1; $^{11}$B NMR
(160 MHz, CDCl₃) δ –5.4 (d, J = 108 Hz); HRMS (ESI, TOF) m/z [M+H]+ calculated for C₁₇H₂₂BN₂O₄ 329.1673, found 329.1687.

ASSOCIATED CONTENT

Supporting Information. Contains details of EPR experiments and calculations with copies of spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENTS

J.C.W. thanks EaStCHEM for financial support and D.P.C. thanks the US National Science Foundation. Computational support was provided through the EaStCHEM Research Computing Facility.

References and Notes


14. This spectrum was obtained somewhat fortuitously when we conducted an experiment with **3d** in *t*-butylbenzene with 5% allyl bromide to see if we could intercept the boraallyl radical by bromine atom abstraction prior to cyclization. This reaction did not occur, and instead we obtained a high quality 2nd derivative spectrum of of the oxaborole radical, which evidently did not react with allyl bromide either.

3082; (b) Studer, A.; Amrein, S., Tin Hydride Substitutes in Reductive Radical Chain Reactions. 


**Table of Contents Graphic**

![Chemical Diagram](attachment:chemical-diagram.png)

- **borallyl radicals**
  - not observed by EPR
- **oxaborole radicals**
  - two conformers observed by EPR
- **boralactones**
  - isolated as stable products