Concentration Studies on the Radical Cyclizations of Enol acetates and Enol carbonates and the Possible Formation of 4-Hydrindanones via an Uncommon Acyl Radical Fragmentation

by

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Concentration Studies on the Radical Cyclizations of Enol acetates and Enol carbonates
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Fragmentation

Tiffany Renee Turner, M.S.

Recently, Uta Wille and coworkers proposed a novel non-chain, self-terminating, oxidative radical cyclization that ends with the uncommon homolytic cleavage of an acyl-oxygen bond to give a ketone and an acyl radical (J. Amer. Chem. Soc. 2002, 124 (1), 14-15). We present the results of our study into this type of unusual radical fragmentation. Our focus was on initiating radical intermediates $53_{a,b}$ thru thermal means using $\text{Bu}_3\text{SnH}$ to produce ketone $54$ as opposed to photo-induced methods used by Wille. In our work, we were unable to produce $54$ in sufficient yields, but we were able to isolate carbonyl compounds $62-63_{\alpha,\beta}$. Based on these results, we cannot rule out an alternative polar fragmentation.
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PREFACE

I am dedicating this thesis to my family, friends and colleagues who have supported me and continue to support me throughout my graduate career. I would have failed miserably if it hadn’t been for the constant urging, pushing and encouragement to succeed. First, to my family for supporting my return to school after three years in industry- your love can’t be measured and the financial support was much needed. You continue to support me and understand that more years of school will allow me to attain my career goals, even when you wonder if I will ever finish school.

Second, to my friends in and out of the Chemistry Department who have kept me sane, given me a shoulder to cry on, a ear to listen and the many cheers and beers for our accomplishments. A very special thanks to Andre Lapierre and Jon Tripp for being the best group members and the best friends a girl could ever have. You helped me excel, made me laugh and lit the fire when I needed it lit. To Marc, Jose and Mancuso, thanks for helping out a lowly grad student when you were the great post docs. To Bobbie, my partner in GK-12 you are a great friend, a great mentor and a great teacher. The Carmalt students are lucky to have you as a science teacher and a role model. To Marv, you are a great friend and I am glad I met you so many years ago. You keep it real and keep my feet planted and pointed in the right direction. To past and present Curran group members, you have provided knowledge, friendship and some unwanted competition and aggravations but it was all worth it- I am who I am because of you.

I cannot thank Drs. Joe Grabowski and George Bandik enough for seeing and promoting my desire to teach chemistry. Your insight and mentorship has been invaluable and will never be forgotten. Without your guidance, I would not have had the opportunities to expand my teaching skills and fall in love with teaching undergraduates the ins and outs of chemistry. I hope to one day be as confident in front of a class and as knowledgeable as you.

Finally, I would like to thank my committee and my advisor for your wisdom and teachings during my time in Pittsburgh. You pushed me to work harder and to realize I will always have more to learn.
1. Introduction

1.1. Self-terminating Oxidative Radicals

There are three general types of reactions for oxygen-centered radicals: hydrogen abstraction, B-C-C fission and C-O bond formation. Dr. Uta Wille has recently demonstrated a new use of oxygen-centered inorganic radicals as oxygen atom donors upon addition to alkyne triple bonds. In a typical example, treatment of cyclodecyne 1 with •OC(O)Me, in benzene or acetonitrile at room temperature, gave cis-fused bicyclic ketones 2 and 3 in 25% combined gc yield (1:1) (Figure 1a). When 1 is in 2-3 fold excess, the combined yield of 2 and 3 increases to 66%. The acyloxy radical 5 was formed by the photolysis of its precursor, Barton ester thiopyridone 4 (Figure 1b).

![Figure 1 a) Reaction of 1 with •OX; b) photolysis of 4](image-url)
When the (alkoxycarbonyl)oxyl radical $\cdotOC(\text{O})\text{OMe}$ is used, the combined yield of 2 and 3 is 94% (1:1) (Table 1, entry 5). These results are consistent with the reaction of 1 with inorganic radicals $\text{NO}_3\cdot$ (Table 1, entry 1), $\text{SO}_4\cdot$ (Table 1, entry 2) and $\cdot\text{OH}$ (Table 1, entry 3). Dr. Wille has also demonstrated the synthetic application of this novel radical cyclization with various cyclic and open chain alkynes.²

Based on these results, a novel self-terminating, oxidative radical cyclization has been proposed by Wille.³ The mechanism starts with addition of an oxygen-centered radical ($\cdot\text{OX}$) to the alkyne to form vinyl radical intermediate 6. 1,5 transannular hydrogen atom transfer (HAT) of Hα forms 7a and is followed by 5-exo cyclization to form 8a. 1,6 transannular HAT of Hβ forms 7b and is followed by 6-exo cyclization to form 8b. Finally, termination of the cascades via β-scission of the α-oxygen radicals forms ketones 2 and 3, from 8a and 8b, respectively. During the β-scission, unreactive

---

**Table 1** Combined Yields of 2 and 3 from cyclodecyne with *OX

<table>
<thead>
<tr>
<th>X</th>
<th>Yield (%)⁷,a,b</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NO}_2$³</td>
<td>70⁷</td>
</tr>
<tr>
<td>$\text{SO}_3$⁵</td>
<td>79⁷</td>
</tr>
<tr>
<td>H⁸</td>
<td>21⁷</td>
</tr>
<tr>
<td>C(O)Me⁹</td>
<td>25⁷ (66)</td>
</tr>
<tr>
<td>C(O)OMe⁹</td>
<td>94⁹</td>
</tr>
</tbody>
</table>

³ Combined yield of cis-2 and cis-3.
⁴ Reaction conditions: Benzene/MeCN at RT.
⁵ Electrogenerated $\text{NO}_3\cdot$.
⁶ Isolated Yield.
⁷ Fenton redox generation of $\text{SO}_4\cdot$.
⁸ Yield with internal standard (n-hexadecane).
⁹ Generated from photolysis of thiopyridinone.

Based on these results, a novel self-terminating, oxidative radical cyclization has been proposed by Wille. The mechanism starts with addition of an oxygen-centered radical ($\cdot\text{OX}$) to the alkyne to form vinyl radical intermediate 6. 1,5 transannular hydrogen atom transfer (HAT) of Hα forms 7a and is followed by 5-exo cyclization to form 8a. 1,6 transannular HAT of Hβ forms 7b and is followed by 6-exo cyclization to form 8b. Finally, termination of the cascades via β-scission of the α-oxygen radicals forms ketones 2 and 3, from 8a and 8b, respectively. During the β-scission, unreactive
inorganic radicals, in the case of $X = \text{NO}_2\cdot$ and $\text{SO}_3\cdot$, are formed. The same pathways are proposed for the reactions of acyloxyl ($\cdot\text{OC(O)Me}$), (alkoxycarbonyl)oxyl ($\cdot\text{OC(O)OMe}$), and hydroxyl ($\cdot\text{OH}$) radicals where the reactive acyl ($\cdot\text{C(O)Me}$), alkoxy carbonyl ($\cdot\text{C(O)OMe}$), and hydrogen ($\cdot\text{H}$) radicals are formed upon fragmentation.

![Chemical diagram](image)

**Figure 2** Mechanism for self-terminating, oxidative radical cyclization proposed by Wille

Known reactions of acyloxyl radicals include decarboxylation of diacyl peroxides,$^4$ hydrogen atom abstraction,$^5$ and addition to aliphatic C-C double bonds.$^6$
We find Wille’s proposed mechanism interesting because it suggests an uncommon radical fragmentation as the terminating step in the cascade shown in Figure 2. The homolytic cleavage of the acyl-oxygen bond and alkoxy carbonyl-oxygen bond in the radical intermediates 8a,b is uncommon.

1.2. Reactions and Formation of Acyl Radicals

There are three common methods for formation of acyl radicals: (a) homolytic cleavage of RC(O)-X bonds, (b) carbonylation of carbon-centered radicals with CO, and (c) fragmentation of C-C bond or CO-C bonds (Figure 3).\textsuperscript{7}

\[ \begin{align*}
\text{(a)} & \quad \text{O} & \quad \text{Bu}_3\text{Sn} & \quad \text{O} & \quad \text{X} \\
\text{X} = \text{H, halogen, chalcogen, metal} & \\
& \quad \text{10} & \quad \text{11}
\end{align*} \]

\[ \begin{align*}
\text{(b)} & \quad \text{R'} & \quad \text{CO} & \quad \text{O} & \quad \text{R'} \\
& \quad \text{12} & \quad \text{13} & \quad \text{14}
\end{align*} \]

\[ \begin{align*}
\text{(c)} & \quad \text{R} & \quad \text{R} & \quad \text{O} & \quad \text{R'} & \quad \text{X'} \\
& \quad \text{15} & \quad \text{14} & \quad \text{11}
\end{align*} \]

Figure 3 Common methods for acyl radical formation

β-Scission reactions to form acyl radicals are known but uncommon. Anson and Montana proposed the formation of acyl radical intermediates when deprotecting benzyl ester 16 with N-bromosuccinimide under neutral conditions (Figure 4).\textsuperscript{8} The initially formed benzyl radical 18 collapses to give the acyl radical 19 that is trapped by N-bromosuccinimide to give the acyl bromide 21, which is hydrolyzed upon workup. The
radical reaction is then propagated by the released Br•. Formation of the acyl bromide via a radical mechanism has been reported by Herman and coworkers but the pathway was found to be a minor one. Anson and Montana did not do a complete study of the mechanism and therefore could not rule out an ionic fragmentation. Benzyl radical 18 is brominated by NBS to form the benzylic brominated intermediate 22. Fragmentation of 22 forms 23 which becomes 21 after reaction with Br⁻ (Figure 5). This ionic mechanism has been proposed before in the NBS promoted cleavage of benzylidene acetals.

![Figure 4 β-scission of carboxybenzyl radical](image)

![Figure 5 Brominated benzylic ionic fragmentation](image)

If Wille’s proposed radical fragmentation of intermediates 8a,b is correct (Figure 2), we can imagine a possible chain mechanism for a radical isomerization of enol esters to 1,3 diketones (Figure 6). Upon addition of the acyl radical 14 to the enolester 23, we
propose the $\alpha$-oxygen intermediate 24. Homolytic fragmentation of the radical will form a 1,3 diketone 25 and the acyl radical 14 that can propagate the reaction.

Figure 6 Proposed radical addition-fragmentation reaction of electron rich alkenes with acyl radicals

Additions of acyl radicals to electron rich alkenes are known (Step 1) and Wille’s work suggests the fragmentation in Step 2 is plausible. The ability to propagate the radical chain by an acyl radical would eliminate the use of toxic chain propagators such as Bu$_3$SnH.

1.2.1. Radical Addition/Fragmentation Reactions

Roberts recently reported the reactions of halogen atom donor 26 with O-tert-alkyl enols 27a-c to give 1,4-dicarbonyl compounds 28a-c under tin free conditions (Figure 7a). The C-C bond formation occurs by a radical-addition fragmentation, as illustrated in Figure 7b.
At the same time, Roepel reported the radical reactions of $\alpha$-phenylselenyl-malonitrile \textbf{33a} and -malonic ester \textbf{33b} with $O$-benzyl enols \textbf{34a,b} (Figure 8, Table 2).$^{13}$
Table 2 Yields of 35a-d from reactions of α-phenylselenyl-malonitiles and –malonic esters 33a,b and O-benzyl enols 34a,b

<table>
<thead>
<tr>
<th>SePh substrate</th>
<th>enol</th>
<th>Product</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>31a</td>
<td>32a</td>
<td>33a</td>
<td>50&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>31a</td>
<td>32b</td>
<td>33b</td>
<td>69&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>31b</td>
<td>32a</td>
<td>33c</td>
<td>71&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>31b</td>
<td>32b</td>
<td>33d</td>
<td>62&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated Yields. <sup>b</sup> AIBN, refluxing benzene, 16h. <sup>c</sup> hυ, CHCl<sub>3</sub>, 12-17h

1.3. Radical Fragmentation on Model System

As an alternative to Wille’s proposed radical fragmentation, we envision an oxidative fragmentation to form ketone 2 (Figure 9). After radical cyclization, oxidation of the radical intermediate 6a to the cationic intermediate 37 would be followed by polar fragmentation to the corresponding ketone 2 and the acyl cation. An alternate pathway is addition of H<sub>2</sub>O to give the same results.

![Alternate oxidative fragmentation mechanism](image)

X = C(O)Me, C(O)OMe, H

Figure 9 Alternate oxidative fragmentation mechanism

In the example of a hydroxyl radical (●OH) acting as the oxygen donor, under oxidative cleavage a proton (H<sup>+</sup>) would be formed as opposed to a highly reactive hydrogen radical (●H).
We chose to study the radical cyclization and fragmentation of acyl enols \textbf{38a-d} under the reducing conditions of Bu$_3$SnH to probe the mechanism and the possibility of competitive fragmentation (Figure 10).

![Diagram of the reaction process involving acyl enols 38a-d leading to cyclization, fragmentation, and HAT (reduction) products 40a,b, 42a,b, 43a, 44a,b, and 41.]

FIGURE 10 Proposed acyl and alkoxy carbonyl enols for fragmentation studies

Under the reducing conditions of Bu$_3$SnH, the possibility of the alternative oxidative fragmentation could be explored. If ketone \textbf{41} is observed at high concentrations of Bu$_3$SnH, then serial dilutions should produce more \textbf{41} because radical fragmentation is independent of Bu$_3$SnH concentration. At high concentrations, the bimolecular HAT of intermediates \textbf{39a,b} with Bu$_3$SnH to form the reduced products \textbf{42a,b} should compete with cyclization to form radical intermediates \textbf{40a,b}. The same competition of HAT and radical fragmentation should be observed in intermediates \textbf{40a,b} with increased formation of \textbf{43a,β} and \textbf{44a,β} and decreased formation of ketone \textbf{41}. At lower
concentrations, the amounts of reduced products 42-44 should decrease because the reduction is dependent on the Bu$_3$SnH concentration. If ketone formation does not increase with decreasing Bu$_3$SnH concentration, then the radical pathway proposed by Wille cannot be the only mechanism responsible for fragmentation. Therefore, an alternative oxidative mechanism cannot be ruled out.

We decided not to study the fragmentation of the exact compounds in Wille’s experiments due to the possibility of competing 1,5 HAT. We expected the formation of products, 48a,b from precursors 45a,b would compete with the formation of ketones 2 and 3 (Figure 11). We chose to incorporate a methyl substituent into substrates 38a-d to eliminate the competing 1,5 HAT.

Figure 11 Competing HAT with radical precursor
2. Results

2.1. Synthesis and fragmentation studies of phenylselenide precursors

Our initial goal was the synthesis of radical precursor 38 via Copper-catalyzed conjugate addition of butenyl magnesium bromide to enone 49 followed by quenching with acetyl chloride gave known enol acetate 50 in 50% yield (Figure 12).\textsuperscript{14} Acyl enone 50 can also be synthesized in a two-step procedure by forming the enol carbonate 51 via conjugate addition of butenyl magnesium bromide to 49 followed by quenching with methyl chloroformate. Reacting 51 with nBuLi, HMPA and acetyl chloride gave 50 in 62% yield over 2 steps. Even though this path gave a higher yield overall of 50, a significant amount of ketone 52 (15%) was formed, and thus was difficult to separate from 50 by conventional methods. We wanted to avoid the use of HMPA for safety reasons and the formation of ketone 52, so the one-step procedure was used. Anti-Markovnikov addition of HX to the terminal alkene in 50\textsuperscript{15} proved unsuccessful under various conditions.

\begin{align*}
\text{CuBr-DMS} & \quad \text{DMS/\text{Et}_2\text{O}} \\
49 & \quad \text{AcCl} \\
\text{BrMg} & \quad \text{CuBr-DMS} \\
49 & \quad \text{DMS/\text{Et}_2\text{O}} \\
\text{BrMg} & \quad \text{CuBr-DMS} \\
49 & \quad \text{DMS/\text{Et}_2\text{O}} \\
\text{ClC(O)OMe} & \quad \text{THF} \\
\text{nBuLi} & \quad \text{HMPA} \\
\text{AcCl} & \quad \text{THF} \\
\text{50} & \quad \text{52, 15\%} \\
\text{50} & \quad \text{52, 15\%} \\
\end{align*}

Figure 12 (1) Synthesis of 52 and potential formation of 38 (2) Alternate two-step procedure for synthesis of 52
To circumvent the difficulty in making 38, we decided instead to synthesize targets 53a-d. By shortening the alkyl chain by one carbon, hydroindenone 54 should be accessible and still a viable precursor for the concentration studies. Like ketones 2 and 3, 54 should be formed in exclusively the cis orientation during radical cyclization (Figure 13).\(^\text{16}\)

\[
\begin{align*}
53a-d \\
a: & \text{R} = \text{Me} \; \text{X} = \text{I} \\
b: & \text{R} = \text{OMe} \; \text{X} = \text{I} \\
c: & \text{R} = \text{Me} \; \text{X} = \text{SePh} \\
d: & \text{R} = \text{OMe} \; \text{X} = \text{SePh}
\end{align*}
\]

Figure 13 Hydroindenone formation

Dihydroxylation of the terminal alkene of 50 with AD mix-\(\alpha\)\(^\text{17}\) produced an intermediate diol that was subsequently cleaved via NaIO\(_4\) oxidation\(^\text{18}\) in THF/H\(_2\)O to give aldehyde 55 in 75% yield over 2 steps. The aldehyde was reduced with NaBH\(_4\) in MeOH to the corresponding alcohol 56 in 78% yield.\(^\text{19}\) Mesylation of alcohol 56 followed by phenylselenide displacement produced the radical precursor 53c in 46% yield over 2 steps (Figure 14).\(^\text{20}\)
Phenyl selenide 53c, was synthesized in 15% overall yield by following the same procedure with enol carbonate 51 (Figure 15).

Figure 14 Synthesis of phenylselenide 53c

Figure 15 Synthesis of phenyl selenide 53d
Compounds 38c,d were also synthesized in a similar manner from 50 and 51 respectively. If the hydroindenone precursors proved worthwhile, then we could expand the study to look at fragmentations that follow 6-exo cyclization v. 5-exo cyclizations. 50 was hydroborated with 9-BBN and H₂O₂ to produce 59 in 59% yield. Mesylation of 59 followed by phenylselenide displacement gave selenyl ether 38c in 56% yield over 2 steps. Selenyl ether 38d was synthesized in same manner as 38d from 51 in 30% overall yield (Figure 16).

![Synthesis of phenyl selenides 38c,d](image)

Figure 16 Synthesis of phenyl selenides 38c,d

Authentic samples of potential side products from the reaction of 53c,d with Bu₃SnH were synthesized independently to aid in analysis (Figure 17). Directly reduced acyl enols 61a,b were synthesized by copper-catalyzed conjugate addition of propyl Grignard to enone 49 and trapping with the corresponding acid chloride in eqn 1. Acetates 62α,β (1.5:1 dr α:β, 95% combined yield) and carbonates 63 α,β (2:1 dr α:β, 68% combined yield) were synthesized by a preparative scale reactions of 38c,d with Bu₃SnH at 0.1 M in eqn 2. The diastereomeric ratios were determined by 1H NMR.
Reduction of the 1.5:1 dr mixture of $62\alpha,\beta$ with LAH in Et$_2$O gave a 1.5:1 dr mixture of alcohols $64\alpha,\beta$ in 50% combined yield after chromatography. Alcohols $64\alpha,\beta$ were oxidized with DMP$^{21}$ to produce ketone 54 in 50% yield (Figure 17 eqn 3).

$$\begin{align*}
49 & \quad \text{BrMg} \quad \text{CuBr-DMS} \\
& \quad \text{DMS/Et}_2\text{O} \\
& \quad \text{RC(O)Cl} \\
\text{61a} & \quad \text{R = Me (68%) } \\
\text{61b} & \quad \text{R = OMe (75%)} \\
\end{align*}$$

(1)

$$\begin{align*}
38c & \quad \text{R = Me} \\
38d & \quad \text{R = OMe} \\
\text{Bu}_3\text{SnH} & \quad \text{AIBN} \\
\text{Benzene} & \quad \text{0.1 M} \\
\text{62a,}\beta & \quad \text{R = Me (1:1.5 dr,95%) } \\
\text{63a,}\beta & \quad \text{R = OMe(1:2 dr, 68%)} \\
\end{align*}$$

(2)

$$\begin{align*}
62\alpha,\beta & \quad \text{LgH} \\
\text{Et}_2\text{O} & \quad \text{DMS} \\
\text{54} & \quad \text{50%} \\
\text{50%} & \quad \text{DMP} \\
\text{DCM} & \quad \text{50%} \\
\end{align*}$$

(3)

Figure 17 Synthesis of authentic samples 61-64 and 54

With phenylselenyl precursors $38\text{c,d}$ and $53\text{c,d}$ and likely products 61-64 and 54 in hand, concentration studies were carried out for the radical cyclizations under reducing conditions. Reactions with each precursor $53\text{c,d}$ were run in triplicate and analyzed by $^1$H NMR spectroscopy and GC before and after submission to reaction conditions with $p$-dimethoxy benzene as an internal standard. Aliquots of precursors $53\text{c,d}$ in C$_6$D$_6$ were added to a sealed tube followed by aliquots of internal standard in C$_6$D$_6$. After stirring for 30 min, AIBN and Bu$_3$SnH were added and the reaction tube was sealed and placed in a preheated 80°C oil bath. In the reaction at 0.1 M with $53\text{c}$, a diasteromeric mixture of cyclized esters $62\alpha,\beta$ were seen (dr 1.5:1) along with directly reduced enol acetate $61\text{a}$.
and a diastereomeric mixture of alcohols $64\alpha,\beta$ (dr 1.5:1), but no significant evidence of ketone 54 was observed by $^1$H NMR spectroscopy or GC (Figure 18, Table 3).\textsuperscript{22}

![Reaction Scheme](image)

**Figure 18 Reaction of 53c under reducing conditions**

**Table 3 GC and $^1$H NMR Yields from reaction with 53c**

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>Yields ($%$)$^a$</th>
<th>62$\alpha,\beta$</th>
<th>54$^b$</th>
<th>64$\alpha,\beta^b$</th>
<th>61a</th>
<th>53c$^e$</th>
<th>Total GC Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>GC 1H NMR</td>
<td>97.4 91.7</td>
<td>0.3</td>
<td>2.0</td>
<td>0.8  1.3</td>
<td>0 0</td>
<td>100.5</td>
</tr>
<tr>
<td>0.01$^e$</td>
<td>GC 1H NMR</td>
<td>52.4 56.7</td>
<td>0.7</td>
<td>2.6</td>
<td>0.2  1</td>
<td>7.5  5.3</td>
<td>63.4</td>
</tr>
<tr>
<td>0.001$^d$</td>
<td></td>
<td>0 0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>49.  50</td>
<td>49.9</td>
</tr>
</tbody>
</table>

$^a$Yields are the averages of 3 runs at each concentration and based on the internal standard, $p$-dimethoxy benzene. $^b$1H NMR yields were not determined due to overlapping resonances. $^c$5% of an unidentified compound was detected. Uncorrected yield based on assumed chemical structure. $^d$10% of an unidentified compound was detected. Uncorrected yield based on assumed chemical structure. $^e$Yields are the % of 53c detected.

By lowering the concentration to 0.01M, significant formation of 54 was not observed. In the reaction at 0.001M did not allow the reaction to proceed with the major component 53c being observed by $^1$H NMR and GC. The formation of an unidentified product was observed at the lower concentrations. Neither the ketone 54 nor the directly reduced product 61a was observed at the lower concentrations. Similar results were seen with radical precursor 53d (Figure 19 and Table 4).\textsuperscript{23} In the reaction at 0.1M, entire
consumption of 53d was observed, but a low yield of 63α,β was seen by 1H NMR and GC. Lowering the concentration to 0.01M showed significant detection of 53d and a slight increase in 63α,β. At the lowest concentration of 0.001M, only detection of 53d was observed. At all three concentrations, ketone 54 was not observed in significant amounts by 1H NMR or GC.

![Reaction diagram](image)

Figure 19 Reaction of 53d under reducing conditions

Table 4 GC and 1H NMR Yields from reaction with 53d

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>Yieldsa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>63α,β</td>
</tr>
<tr>
<td></td>
<td>GC 1H NMR</td>
</tr>
<tr>
<td>0.1</td>
<td>45.5 47.7</td>
</tr>
<tr>
<td>0.01c</td>
<td>51.5 54</td>
</tr>
<tr>
<td>0.001d</td>
<td>0 0 0</td>
</tr>
</tbody>
</table>

aYields are the averages of 3 runs at each concentration and based on the internal standard, p-dimethoxy benzene. b1H NMR yields were not determined due to overlapping resonances. c6.7% of an unidentified compound was detected. Uncorrected yield based on assumed chemical structure. d7.7% of an unidentified compound was detected. Uncorrected yield based on assumed chemical structure. eYields are the % of 53d detected.

Based on these findings, the rates of cyclization for radical precursors 38c,d were faster than the rates of hydrogen abstraction to form 61a,b, respectively. The rate constant of H abstraction by radical 65 from Bu3SnH was calculated to be less than 4.3 x 10⁶ M⁻¹ s⁻¹ at 80°C in benzene using the determined Arrhenius parameters for the rate of
H abstraction from Bu$_3$SnH of primary C radical 65 (Figure 20).$^{24}$ The rate constant was
calculated based on a primary C radical because an appropriate value for a tertiary C
radical next to an ester could not be found. The actual rate is probably slower due to the
increased stability of a tertiary radical over a primary radical.

\[
\begin{align*}
\text{H}_2\text{CO} & \quad \text{Bu}_3\text{SnH} \quad \text{MeO} \\
65 & \quad \text{k} = 4.3 \times 10^6 \text{ M}^{-1}\text{s}^{-1} \quad (1) \\
\end{align*}
\]

\[
\begin{align*}
\text{OAc} & \quad \text{H} \\
67 & \quad \text{k} \leq 4.3 \times 10^6 \text{ M}^{-1}\text{s}^{-1} \quad (2)
\end{align*}
\]

**Figure 20 H abstraction rate constants**

Formation of the alcohols 64$^{\alpha,\beta}$ can potentially be explained by reduction of the
54 with HSePh, a side product in the reaction. The unidentified product formed at lower
concentrations was assumed to be 68 (Figure 21). This assumption was based on $^1$H
NMR and GCMS data of the crude reaction mixture. $^1$H NMR spectrum shows a
multiplet between 5.70 and 5.83 ppm (integrates for 1 H) that is coupled to a multiplet
between 4.92 and 5.03 ppm (integrates for 2 H). The pattern is similar to the $^1$H NMR
spectrum of olefin 50. GCMS data shows an ion peak at 152 which is consistent with the
molecular weight of 68. A fragment peak is seen at 111 which can correspond to the loss
of C$_3$H$_5$. Unfortunately, an authentic sample of 68 was never successfully synthesized or
isolated from the reaction mixture. Instead of forming the primary radical under the
conditions, trace amounts of O$_2$ can promote selenoxide elimination to form the olefin.
This result was confirmed by a model reaction of dodecyl phenylselenide 69 at 0.001 M
under standard reducing conditions and formation of dodecene 70 by $^1$H NMR and GC.
2.2. Synthesis and fragmentation Studies of iodo precursors

Since we felt the presence of PhSeH or PhSeOH might compromise the results, precursors 38c,d were not subjected to the reaction conditions. We decided instead to change the radical precursor to iodides 53a,b to eliminate the problems seen with the phenylselenide precursors. Starting with alcohol 56, mesylation followed by displacement gave iodide 53a in 73% yield over 2 steps. The same procedure was used to produce iodide 53b from alcohol 58 in 68% yield over 2 steps (Figure 22).

Figure 22 Formation of iodides 53a,b

Primary iodides 53a,b have the potential to cyclize by a polar pathway upon heating under the reaction conditions instead of a radical pathway so both iodides were heated to 120°C in C₆D₆ for 24 h at 0.1M to observe any decomposition or cyclization (Figure 23, Table 5). After 24 h, neither ketone 54 nor decomposition of iodides 53a,b was observed and iodides 53a,b were observed in >99% yield by ¹H NMR and GC.
Figure 23 Possible polar cyclization of 53a,b to give ketone 54

Table 5 Yields of decomposition or cyclization of 79 and 80 via a polar pathway conditions

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Yield</th>
<th>SM</th>
<th>1H NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM Iodide</td>
<td>GC</td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>53a</td>
<td>0</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>53b</td>
<td>0</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

a Yields based on internal standard, p-dimethoxybenzene. b 1H NMR yields were not determined due to overlapping resonances.

Following the same protocol for the reaction of 38c,d under Bu₃SnH reducing conditions, iodides 53a,b were monitored by ¹H NMR spectroscopy and GC for formation of ketone 54.

Figure 24 Reaction of 53b to produce 63α,β and 54
Table 6 GC and $^1$H NMR Yields from reaction with 53b

<table>
<thead>
<tr>
<th>Conc.  (M)</th>
<th>Yields$^a$</th>
<th>63$\alpha,\beta$</th>
<th>1H NMR</th>
<th>54$^b$</th>
<th>53b</th>
<th>Total GC Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>GC</td>
<td></td>
<td>GC</td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>80</td>
<td>73</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>82</td>
</tr>
<tr>
<td>0.01</td>
<td>70</td>
<td>80</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>71</td>
</tr>
<tr>
<td>0.001</td>
<td>60</td>
<td>55</td>
<td>1</td>
<td>25</td>
<td>30</td>
<td>86</td>
</tr>
</tbody>
</table>

$^a$Yields are based on the internal standard, p-dimethoxy benzene. $^1$H NMR yields were not determined due to overlapping resonances.

Yields are the % of 53b detected.

For 53b, the reactions were not run in triplicate because the initial reactions at each concentration only produced the diastereomeric mixture of cyclized carbonates, 63$\alpha,\beta$ and very little 54 (Figure 24, Table 6). The directly reduced enol carbonate 61b and alcohols 64$\alpha,\beta$ were not observed. Figure 25 and 26 show representative spectra of the reaction at 0.1M.
Figure 25 1H NMR spectrum of 63α,β
Figure 26 GC spectrum of 63α,β and 54

With iodide 53a, an additional concentration of 0.005 M was added because an appreciable amount of ketone 54 was observed by GC (Figure 27, Table 7).26 Again, the cyclized acetates 62α,β (dr 3:1) were formed as the major products and directly reduced 61a and alcohols 64α,β were not observed with this system. Figure 28 and 29 show representative spectra of the reaction at 0.1M.

Figure 27 Reaction of 53a to produce 62α,β and 54
Table 7 GC and $^1$H NMR Yields from reaction with 53a

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>Yields$^a$</th>
</tr>
</thead>
</table>
| | 62α,β | 54$^b$ | 53a$^c$ | Total GC Yield  
| | GC | $^1$H NMR | GC | $^1$H NMR |  
| 0.1 | 94.8 | 95.3 | 2.4 | 0 | 0 | 97.2  
| 0.01 | 73 | 73 | 7.5 | 0 | 0 | 80.5  
| 0.005 | 28.3 | 30 | 15.6 | 42.1 | 38.7 | 86.0  
| 0.001 | 1.2 | 0 | 15.6 | 42.9 | 41 | 59.7  

$^a$Yields are the averages of 3 runs at each concentration and based on the internal standard, $p$-dimethoxy benzene. $^b$1H NMR yields were not determined due to overlapping resonances. $^c$Yields are the % of 53a detected.

Decreasing the concentration of Bu$_3$SnH did show an increase in the formation of 54 with 7.5% at 0.01M to 15.6% at 0.005M and 0.001M. This increase was not enough to rule in favor of the radical fragmentation pathway proposed by Wille or the alternative oxidative pathway proposed by us.
Figure 28 1H NMR spectrum of $62\alpha,\beta$
2.3. Oxidation in a reducing environment

The question arose during our studies, how does oxidation occur in a reducing environment? Studies have been done that probe this question but the mechanism is still not thoroughly understood.\(^\text{27}\) One explanation can be the initiator, AIBN, acting as the oxidant.\(^\text{28}\) To probe this possibility, varying equivalents of AIBN were added to the reaction of \(53\text{a} \) at 0.01M and monitored by \(^1\text{H} \text{NMR} \) and GC (Figure 27). Instead of an increase in ketone formation, we noticed a slight decrease in yield of the ketone \(54\) with increasing amounts of AIBN (Table 8). From this we can conclude that AIBN is not the oxidant during the reaction.

Figure 29 GC spectrum of \(62\alpha,\beta\) and 54
Table 8 GC and $^1$H NMR Yields from reaction with 53a

<table>
<thead>
<tr>
<th>AIBN (equiv)</th>
<th>$62\alpha,\beta$</th>
<th>$^1$H NMR</th>
<th>$54^b$</th>
<th>Total GC Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GC</td>
<td>GC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>73.1</td>
<td>69.0</td>
<td>12.4</td>
<td>85.5</td>
</tr>
<tr>
<td>0.5</td>
<td>71.4</td>
<td>73</td>
<td>14.7</td>
<td>86.1</td>
</tr>
<tr>
<td>.75</td>
<td>76.4</td>
<td>73.3</td>
<td>10.1</td>
<td>86.5</td>
</tr>
<tr>
<td>1.00</td>
<td>76.6</td>
<td>71.1</td>
<td>7.8</td>
<td>84.4</td>
</tr>
<tr>
<td>2.00</td>
<td>71.0</td>
<td>69.0</td>
<td>8.7</td>
<td>79.7</td>
</tr>
</tbody>
</table>

$^a$Yields are based on the internal standard, $p$-dimethoxy benzene.

$^b$H NMR yields were not determined
2.4. Conclusions

After our studies were completed, Sigmung, Schiesser and Wille published their findings of a theoretical and experimental investigation of the terminating homolytic fragmentation of the O-X bond in 71 where X is alkyl, aromatic or allyl as seen in Figure 30. They wanted to provide insight into the energetic requirements and driving forces of the final fragmentation step.

Figure 30 homolytic fragmentation of the O-X bond

For the experimental portion of the study, the alkoxy radicals were generated in the presence of cyclodecyne 1 by the photolysis of the dithiocarbamate precursors 75 (Figure 31, Table 9).
Unlike previous studies, the solvent was switched from benzene to acetone and the ratio of radical precursor to alkyne was increased from 3:1 to 2:1. Acetone was found to be a superior solvent to benzene and it was speculated that the acetone diradical formed upon UV irradiation could either add to or transfer its triplet character to the radical precursor, initiating formation of the alkoxyl radicals. This hypothesis is supported by the absence of initiator AIBN in the reaction. The yields were similar to the yields when using the inorganic nitrate radicals and sulfate radical anions but they were surprised that alkoxyl allyl radical had a lower yield than the n-butyl alkoxyl radical. One would expect the alkoxyl radical with a stabilized leaving group (allyl) upon scission would be better than the nonstabilized n-butyl fragment.

The theoretical calculations were carried out for the simplified model reaction shown in Figure 30. Representative groups were investigated using various methods: methyl, ethyl (non-stabilized radicals), t-butyl (inductive effect stabilized radicals), allyl and benzyl (resonance stabilized radicals). Trends were observed for \( \Delta E^\dagger \) and \( \Delta E \) depending on the stabilization of the radical and were opposite to the observed experimental yields. Resonance stabilized radicals make the hemolytic scission thermodynamically and kinetically favorable whereas inductive stabilization only lowers the activation barrier. The non-stabilized radicals were seen to be both kinetically and
thermodynamically unfavorable as one would expect. The following explanations were presented to account for the discrepancies between the experimental and theoretical data:

(1) The theoretical investigations are calculated in the gas phase and the experimental investigations are in solution and therefore can be directly compared.

(2) The homolytic O-X fragmentation is only one of several steps in the pathway, which may be all of similar importance for the overall success of the reaction.

(3) The homolytic bond cleavage may be an ionic fragmentation (Figure 32). Even though the cleavage of O-NO$_2$ was theoretically verified, the same mechanism may not be favored for reactive radicals (allyl, benzyl, acyl). The nature of the oxidant is unknown and photoexcited acetone cannot be excluded.

Based on our findings, we also conclude the terminating step of the mechanism is more than likely not the homolytic cleavage of O-X but an oxidative fragmentation of the a-oxygen radical or a combination of the two. As in Wille’s observations and ours, the nature of the oxidant is unknown.
3. Experimental

General Procedures:

All reactions were performed under an atmosphere of argon unless the reaction solvent contained water. The reaction times reported are dictated by TLC analysis of the reaction mixture in comparison to the starting material. Reaction solvents were dried either by distillation or passing through an activated alumina column. Methylene chloride was distilled from CaH$_2$ and toluene, benzene, diethyl ether and THF were distilled from Na/benzophenone. Solvents dried by activated alumina were done according to Pangborn, A.B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics, 1996, 15, 1518-1520.

$^1$H and $^{13}$C NMR spectra were taken on a Bruker models Avance DPX 300 (300 MHz), Avance 300 (300 MHz), Avance DRX 500 (500 MHz), or Avance 600 (600 MHz) NMR spectrometer. Chemical shifts are reported in parts per million (ppm) downfield relative to TMS using the residual solvent proton resonance of CDCl$_3$ (7.27 ppm) or central CDCl$_3$ carbon peak (77.0 ppm) as an internal standard or C$_6$D$_6$ (7.15 ppm for $^1$H and 128.0 ppm for $^{13}$C). In reporting spectral data the format (δ) chemical shift (multiplicity, J values in Hz, integration) was used with the following abbreviations: s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, sext = sextet, m = complex multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublets of doublets.

Infrared spectra were taken on a Mattson Genesis Series FTIR using thin film or neat deposition on NaCl plates. Peaks are reported in wavenumbers (cm$^{-1}$). Low and high resolution electron impact mass spectra were obtained on a Micromass Inc, Autospec with an E-B-E geometry. Chemical ionization spectra were taken on the same instrument using methane as the carrier gas. All peaks reported are in units of m/e.

Gas chromatograms (GC) were run on an Agilent 6850 Series GC System with an HP-1 Methyl Siloxane column (Agilent 19091Z-413E, Capillary 30.0 m x 320 µm x 0.25µm). The initial temperature of the program was 150 °C with a temperature ramp of 5°C/min up to 250 °C a helium flow of 2 mL/min and 8.68 PSI was applied. p-dimethoxybenzene was used as internal standard and C$_6$D$_6$ or benzene was used as solvent. GC data are reported with a retention time and % area of the total integrated area.
Thin layer chromatography was performed on silica gel 60 F$_{254}$ glass backed plates with a layer thickness of 0.25 mm manufactured by E. Merck. TLC visualization was performed by illumination with a 254 nm UV lamp or by staining with phosphomolybdic acid or permanganate solution and subsequent heating. Flash chromatography was performed on silica gel (230 – 400 mesh ASTM) purchased from Sorbtech or Bodman.
Acetic acid 3-but-3-enyl-3-methyleyclohex-1-enyl ester (50).  

Preparation of the Grignard reagent: Magnesium (0.40 g, 16.3 mmol) and a crystal of iodine were placed in a dry three-neck 50 mL round bottom flask attached to a reflux condensor and addition funnel. The contents were flame dried and cooled under argon. 4-Bromo-1-butene (1.38 mL, 13.62 mmol) in dry Et₂O (20 mL) was added dropwise over 10 min via addition funnel and the mixture was refluxed for an additional 10-15 min and then cooled.

To a dry three-neck 125 mL round bottom flask, attached to a reflux condensor and addition funnel, was added CuBr • DMS (0.19 g, 0.91 mmol), 49 (1.03 mL, 9.08 mmol) and dry DMS/ether (40 mL, 50:50) under argon. The solution was cooled to 0°C and the Grignard reagent was transferred via cannula to the addition funnel and added dropwise over 1 h. The mixture was warmed to RT after addition for 1 h and then recooled to 0°C. Acetyl chloride (3.20 mL, 45.4 mmol) was added and the mixture was then allowed to stir at RT overnight under argon. The reaction mixture was quenched with sat’d NH₄Cl (10 mL) and the layers were separated. The aqueous layer was extracted with Et₂O (20 mL), the combined organic layers were washed with sat’d NH₄Cl (4 x 20 mL), dried over MgSO₄ and concentrated in vacuo. The crude mixture was purified by column chromatography (98:2 Hexanes:EtOAc) to give 50 (0.95 g) as clear oil in 50% yield. Characterization data matches literature values. ¹H NMR (300 MHz, CDCl₃) δ 5.78 (ddddd, J = 17.3, 13.1, 10.1, 6.8 Hz, 1H), 5.11 (s, 1H), 4.94 (dd, J = 17.3, 1.9 Hz, 1H), 4.90 (dd, J = 10.1, 1.9 Hz, 1H), 1.95-2.16 (m, 4H), 2.06 (s, 3H), 1.69-1.77 (m, 2H), 1.30-1.55 (m, 4H), 1.01 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 168.6, 147.2, 138.8, 122.3, 133.7, 41.6, 34.4, 33.8, 28.2, 27.0, 26.6, 20.6, 19.1; IR (neat) 1755, 1686, 1363 cm⁻¹; LRMS (EI) (M — CH₃) 193, 151. 111, 84 m/e; HRMS (EI) cal’d for 193.122183, found 193.122185.

Acetic acid 3-methyl-3-(3-oxopropyl)cyclohex-1-enyl ester (55).  

To a 50 mL round bottom flask equipped with a stirrer was added H₂O (10 mL), t-butanol (10 mL), and AD mix-α (3.36 g) and the mixture stirred vigorously at RT for 0.5 h until 2 clear layers were formed. The mixture was cooled to 0°C and 50 (0.50 g, 2.23 mmol) was added neat and the mixture was stirred at RT overnight. Solid sodium sulfite
(3.60 g) was added to the mixture and stirred for an additional 30 min. The suspension was diluted with DCM (25 mL) and layers separated. The aqueous layer was extracted with DCM (3 x 15 mL), dried over MgSO$_4$ and concentrated in vacuo to give the diol as a clear yellow oil that was used in the next step without further purification. **Diol:** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.07 (s, 1H), 3.56-3.59 (m, 2H), 3.37-3.41 (m, 1H), 2.9 (bs, 2H), 2.04-2.12 (m, 2H), 2.08 (s, 3H), 1.71-1.75 (m, 2H), 1.26-1.40 (m, 6H), 0.91 (s, 3H).

To a 50 mL round bottom flask was added the diol, NaIO$_4$ (0.51 g, 2.36 mmol) and THF/H$_2$O (16 mL, 3:1 ratio) and the reaction mixture was stirred at RT overnight. The resulting mixture was poured into H$_2$O (10 mL) and extracted with Et$_2$O (5 x 20 mL). The organic layers were combined, dried over MgSO$_4$ and concentrated in vacuo. The crude mixture was purified by flash chromatography (80:20 Hexanes: EtOAc) to give aldehyde **55** as a clear oil (0.35 g) in 75% yield over 2 steps. Characterization data matches literature values. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.59 (s, 1H), 4.88 (s, 1H), 2.29 (t, $J$ = 7.8 Hz, 1H), 1.79-2.00 (m, 2H), 1.91 (s, 3H), 1.45-1.62 (m, 4H), 1.28-1.39 (m, 2H), 0.85 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 201.9, 168.6, 147.8, 121.4, 38.9, 34.0, 33.6, 33.3, 27.0, 26.4, 20.5, 18.9.

**Acetic acid 3-(3-hydroxypropyl)-3-methylcyclohex-1-enyl ester (56).**

To a stirred solution of aldehyde **55** (0.40 g, 1.77 mmol) in MeOH (2.5 mL) at 0°C was added NaBH$_4$ (63.0 mg, 1.68 mmol) portionwise. The mixture was allowed to stir under argon for 1 h at 0°C and then diluted with H$_2$O (6 mL) and extracted with DCM (4 x 5 mL). The organic layers were combined, dried over MgSO$_4$, and concentrated in vacuo. The crude mixture was chromatographed (80:20 Hexanes:EtOAc) to give alcohol **56** as a clear oil (314 mg, 78% yield).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.02 (s, 1H), 3.48 (t, $J$ = 6.1 Hz, 2H), 2.58 (bs, 1H), 2.00 (s, 3H), 1.90-2.02 (m, 2H), 1.65 (q, $J$ = 5.8 Hz, 2H), 1.22-1.48 (m, 6H), 0.92 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 169.3, 147.2, 122.7, 66.0, 38.4, 34.3, 33.8, 27.2, 27.1, 26.6, 20.9, 19.2; IR (neat) 3368, 1754 cm$^{-1}$; LRMS (EI) (M- C$_2$H$_2$O) 170, 153, 137, 111 m/e; HRMS (EI) cal’d for C$_{10}$H$_{18}$O$_2$ 170.13068, found 170.12998.
Acetic acid 3-methyl-3-(3-phenylselanylpropyl)cyclohex-1-enyl ester (53c).

To a solution of alcohol 56 (314 mg, 1.29 mmol) and Et$_3$N (0.27 mL, 1.94 mmol) in DCM (5 mL) at 0°C was added mesyl chloride (0.13 mL, 1.64 mmol). The solution was allowed to stir at 0°C under argon for 3 h then poured into a mixture of H$_2$O (5 mL) and Et$_2$O (12 mL). The aqueous layer was separated and extracted with Et$_2$O (3 x 12 mL). The organic layers were combined and washed with H$_2$O (10 mL), brine (10 mL) and then dried over MgSO$_4$ and concentrated in vacuo to give the mesylate as a yellow oil. The crude mesylate was used in the following step without further purification.

**Mesylate:** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.01 (s, 1H), 4.10 (t, $J = 6.5$ Hz, 2H), 2.91 (s, 3H), 1.96-2.03 (m, 2H), 2.00 (s, 3H), 1.61-1.68 (m, 4H), 1.26-1.41 (m, 4H), 0.93 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 168.7, 147.5, 121.8, 59.9, 37.8, 36.7, 33.4, 26.9, 26.4, 23.7, 20.6, 18.9, 13.8.

To a solution of diphenyldiselenide (842 mg, 2.4 mmol) in dry DMF (10 mL) at 0°C was added NaBH$_4$ (184 mg, 4.8 mmol) portionwise. After the evolution of hydrogen ceased, the mesylate (327 mg, 1.13 mmol) in DMF (20 mL) was added dropwise and the mixture was stirred at RT under argon for 4 h. The reaction was quenched with H$_2$O (20 mL) and extracted with EtOAc (5 x 50 mL). The organic layers were combined, dried over MgSO$_4$ and concentrated in vacuo. Chromatography (gradient elution 100% Hexanes-10% EtOAc) gave selenyl ether 53c (238 mg, 46 % yield over 2 steps) as a yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.52-7.54 (m, 2H), 7.28-7.31 (m, 3H), 5.15 (s, 1H), 2.94 (t, $J = 7.2$ Hz, 2H), 2.13-2.16 (m, 2H), 2.15 (s, 3H), 1.70-1.85 (m, 4H), 1.30-1.55 (m, 4H), 1.04 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 169.0, 147.4, 132.3 (2C), 130.5, 128.8 (2C), 126.5, 122.5, 42.6, 34.6, 33.9, 28.5, 27.1, 26.7, 24.6, 20.9, 19.2; IR (neat) 2933, 1436 cm$^{-1}$; LRMS (EI) 352, 310, 111 m/e; HRMS cal’d for C$_{18}$H$_{24}$O$_2$Se 352.09415, found 352.09378.

Acetic acid 3-(3-iodopropyl)-3-methylocyclohex-1-enyl ester (53c).

Following the procedure to form mesylate, alcohol 56 (540 mg, 2.55 mmol) gave the mesylate (740 mg, 2.55 mmol). To a solution of mesylate in acetone (36 mL) was added NaI (384 mg, 2.56 mmol) and the mixture was allowed to reflux under argon for 2.5 h.
The mixture was cooled to RT and the acetone was evaporated in vacuo. The solid mixture was dissolved in H₂O (10 mL) and extracted with DCM (3 x 10 mL). The organic layers were combined and dried over MgSO₄ and concentrated in vacuo. Chromatography (90:10 Hexanes:EtOAc) gave iodide 53c (593 mg, 73% yield 2 steps).

1H NMR (300 MHz, C₆D₆) δ ~ . .1 .. . . . . . . . . . . . . .1 .. . . . .1 , 1.10-1.03 (m, 4H), 0.78 (s, 3H); 13C NMR (75 MHz, C₆D₆) δ 168.4, 148.2, 122.5, 43.5, 34.5, 34.1, 28.8, 27.4, 27.2, 20.6, 19.6, 7.38; IR (neat) 1754, 1218 cm⁻¹.

**Carbonic acid 3-but-3-enyl-3-methylcyclohex-1-enyl ester methyl ester (51).**

Carbonate 51 was prepared in the same manner as acetate 50 using methyl chloroformate (3.51 mL, 45.4 mmol). The crude mixture was purified by column chromatography (98:2 Hexanes:EtOAc) to give 1.2 g of the carbonate in 58% yield. Characterization data matches literature values.

1H NMR (300 MHz, CDCl₃) δ 5.84 (dddd, J = 16.5, 13.5, 10.5, 6.8 Hz, 1H), 5.23 (s, 1H), 5.05 (dd, J = 16.5, 1.5 Hz, 1H), 4.95 (dd, J = 10.5, 1.5 Hz, 1H), 3.82 (s, 3H), 2.15-2.21 (m, 2H), 2.03-2.11 (m, 2H), 1.75-1.85 (m, 2H), 1.36-1.61 (m, 4H), 1.06 (s, 3H); 13C NMR (75 MHz, CDCl₃) δ 154.1, 147.8, 139.2, 122.8, 114.1, 54.8, 41.8, 34.8, 34.0, 28.6, 27.2, 26.5, 19.2; IR (neat) 1759, 1441 cm⁻¹; LRMS (EI) 224, 169, 125, 84 m/e; HRMS (EI) cal’d for C₁₃H₂₀O₃ 224.14125, found 224.14119.

**Carbonic acid methyl ester 3-methyl-3-(3-oxopropyl)cyclohex-1-enyl ester (57).**

Aldehyde 57 (0.73 g) was prepared in 72% yield over 2 steps in the same manner as aldehyde 55 using carbonate 51 (1.0 g, 4.46 mmol). Characterization data matches literature values. **Diol:** 1H NMR (300 MHz, CDCl₃) δ 5.16 (s, 1H), 3.74 (s, 3H), 3.53-3.57 (m, 2H), 3.32-3.38 (m, 1H), 2.06-2.10 (m, 2H), 1.68-1.71 (m, 2H), 1.26-1.47 (m, 6H), 0.95 (s, 3H). 57: 1H NMR (300 MHz, CDCl₃) δ 9.76 (s, 1H), 5.17 (s, 1H), 3.78 (s, 3H), 2.40-2.46 (m, 2H), 2.11-2.14 (m, 2H), 1.73-1.77 (m, 2H), 1.62-1.67 (m, 2H), 1.38-1.42 (m, 2H), 1.02 (s, 3H); 13C NMR (75 MHz, CDCl₃) δ 201.6, 153.3, 147.9, 121.2, 54.2, 38.6, 33.8, 33.4, 33.0, 26.6, 25.8, 18.7.
Carbonic acid 3-(3-hydroxypropyl)-3-methylcyclohex-1-enyl ester methyl ester (58).

Alcohol 58 (508 mg, 69 % yield) was prepared in the same manner as alcohol 56 from aldehyde 57 (0.73 g, 3.23 mmol). $^1$H NMR (300 MHz, CDCl$_3$) δ 5.02 (s, 1H), 3.56 (s, 3H), 3.34 (t, $J = 6.3$ Hz, 2H), 1.91-1.94 (m, 2H), 1.53-1.57 (m, 2H), 1.11-1.35 (m, 6H), 0.80 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 153.6, 147.1, 122.4, 62.4, 54.3, 38.1, 34.0, 33.4, 26.8, 26.6, 25.9, 18.8; IR (neat) 3345, 2938, 1441 cm$^{-1}$; LRMS (EI) (M-CH$_3$) 213, 195, 169, 125 m/e; HRMS (EI) cal’d for C$_{11}$H$_{17}$O$_2$ 213.1268, found 213.11282.

Carbonic acid methyl ester 3-methyl-3-(3-phenylselanylpropyl)cyclohex-1-enyl ester (53d).

Selenyl ester 53d (253 mg) was prepared in 37% yield over 2 steps in the same manner as 53c using alcohol 58 (430 mg, 1.77 mmol). Mesylate: $^1$H NMR (300 MHz, CDCl$_3$) δ 5.05 (s, 1H), 4.03 (t, $J = 6.4$ Hz, 2H), 3.61 (s, 3H), 2.86 (s, 3H), 1.94-1.99 (m, 2H), 1.55-1.61 (m, 4H), 1.19-1.34 (m, 4H), 0.86 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 153.4, 147.7, 121.7, 70.3, 54.3, 37.6, 36.6, 34.0, 33.2, 26.7, 25.9, 23.6, 18.8. 53d: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.48-7.48 (m, 2H), 7.25-7.22 (m, 3H), 5.19 (s, 1H), 3.78 (s, 3H), 2.87 (t, $J = 7.1$ Hz, 2H), 2.12-2.11 (m, 2H), 1.74-1.64 (m, 4H), 1.46-1.34 (m, 4H), 0.97 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 153.7, 147.5, 132.1 (2C), 130.3, 128.7 (2C), 126.3, 122.4, 54.5, 42.4, 34.5, 33.7, 28.3, 26.9, 26.1, 24.4, 19.1; IR (neat) 2934, 2860, 1689, 1439 cm$^{-1}$; LRMS (EI) 368, 326, 169, 135, 125 m/e; HRMS (EI) C$_{19}$H$_{24}$O$_3$Se cal’d for 368.08907, found 368.08959.

Carbonic acid 3-(3-iodopropyl)-3-methylcyclohex-1-enylester methyl ester (53b).

Iodo 53b (739 mg) was prepared in 68% yield in the same manner as 53a using alcohol 58 (585 mg, 2.56 mmol). $^1$H NMR (300 MHz, C$_6$D$_6$) δ ~11 .1 .3.32 (s, 3H), ~2 .. ~.. .. .. ~10 .5 .. ~1 .. 7i39 .. , 1.09-0.98 (m, 4H), 0.79 (s, 3H); $^{13}$C NMR (75 MHz, C$_6$D$_6$) δ 153.8, 148.7, 123.0, 55.6, 44.1, 35.0, 34.7, 29.3, 27.9, 27.7, 19.9, 8.0; IR (neat) 1750, 1220 cm$^{-1}$. 

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Acetic acid 3-(4-hydroxybutyl)-3-methyl-cyclohex-1-enyl ester (59).

To a solution of alkene 50 (50mg, 0.22 mmol) in THF (0.5 mL) was added 1M solution of 9-BBN in THF (0.56 mL, 0.28 mmol) and the mixture was allowed to stir at RT under argon for 24 h. The mixture was treated with pH 7 phosphate buffer (0.25 mL), a 1:1 solution of THF/EtOH (0.5 mL total), and 30% H$_2$O$_2$ solution (0.5 mL) and allowed to stir for 24h. The reaction mixture was extracted with Et$_2$O (3 x 10 mL) and the combined organic layers were washed with H$_2$O (5 mL) and brine (5 mL). The organic layer was dried over MgSO$_4$ and concentrated in vacuo. Column chromatography of the crude mixture (80:20 Hexanes:EtOAc) gave 59 (32.4 mg) as a yellow oil in 59 % yield.


1H NMR (300 MHz, CDCl$_3$) δ 5.07 (s, 1H), 3.58 (t, $J = 6.5$ Hz, 2H), 2.07 (s, 3H), 2.00-2.06 (m, 2H), 1.67-1.71 (m, 2H), 1.41-1.51 (m, 4H), 1.25-1.33 (m, 4H), 0.95 (s, 3H); 13C NMR (75 MHz, CDCl$_3$) δ 169.4, 147.3, 122.9, 62.7, 42.4, 34.7. 33.9, 33.3, 27.2, 26.7.

Acetic acid 3-methyl-3-(4-phenylselanylbutyl) cyclohex-1-enyl ester (38c).

Selenyl ester 38c (535 mg) was prepared in 56% yield over 2 steps in the same manner as 53c using alcohol 59 (550 mg, 2.6 mmol). Mesylate: 1H NMR (300 MHz, CDCl$_3$) δ 4.95 (s, 1H), 4.06 (t, $J = 6.5$ Hz, 2H), 2.85 (s, 3H), 1.95 (s, 3H), 1.89-1.93 (m, 2H), 1.54-1.60 (m, 4H), 1.16-1.33 (m, 6H), 0.85 (s, 3H); 13C NMR (75 MHz, CDCl$_3$) δ 168.7, 147.1, 122.1, 69.8, 41.6, 36.6, 4.3, 33.5, 29.3, 26.8, 26.4, 20.6, 19.6, 18.9.

38c: 1H NMR (300 MHz, CDCl$_3$) δ 7.45-7.48 (m, 2H), 7.25-7.22 (m, 3H), 5.09 (s, 1H), 2.87 (t, $J = 7.4$ Hz, 2H), 2.11 (s, 3H), 2.06-2.09 (m, 2H), 1.63-1.72 (m, 4H), 1.26-1.44 (m, 6H), 0.97 (s, 3H); 13C NMR (75 MHz, CDCl$_3$) δ 168.6, 147.0, 131.9 (2C), 130.3, 128.5 (2C), 126.2, 122.4, 41.8, 34.3, 33.7, 30.5, 27.3, 26.9, 26.5, 23.9, 20.6, 19.0; LRMS (EI) 366, 213, 111 m/e; HRMS (EI) C$_{19}$H$_{26}$O$_2$Se cal’d for 366.10980, found 366.11052.

Carbonic acid 3-(4-hydroxybutyl)-3-methylcyclohex-1-enyl ester methyl ester (60).

Alcohol 60 (435 mg, 80.5 % yield) was prepared in the same manner as alcohol 59 from alkene 51 (0.5 g, 2.23 mmol). 1H NMR (300 MHz, CDCl$_3$) δ 5.15 (s, 1H), 3.70 (s, 3H), 3.52 (t, $J = 6.5$ Hz, 2H), 2.01-2.07 (m, 2H), 1.64-1.70 (m, 2H), 1.37-1.44 (m, 4H), 1.20-1.35 (m, 4H), 0.92 (s, 3H); 13C NMR (75 MHz, CDCl$_3$) δ 153.9, 147.3, 122.9,
62.4, 54.6, 42.3, 34.6, 33.7, 33.2, 26.9, 26.2, 20.1, 19.2; LRMS (EI) (M-CH3) 227, 169, 125 m/e; HRMS (EI) cal’d for C12H19O4 227.12833, found 227.12841.

**Carbonic acid methyl ester 3-methyl-3-(4-phenylselenylbutyl) cyclohex-1-enyl ester (38d).**

Selenyl ester 38d (253 mg) was prepared in 37% yield over 2 steps in the same manner as 38c using alcohol 60 (430 mg, 1.77 mmol). **Mesylate:** 1H NMR (300 MHz, CDCl3) δ 5.11 (s, 1H), 4.10 (t, J = 6.4 Hz, 2H), 3.67 (s, 3H), 2.89 (s, 3H), 1.99-2.02 (m, 2H), 1.60-1.68 (m, 4H), 1.21-1.40 (m, 6H), 0.90 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 170.6, 147.5, 122.2, 69.9, 59.6, 41.6, 36.6, 34.4, 33.5, 29.3, 26.7, 25.9, 19.6, 18.9.

38d: 1H NMR (300 MHz, CDCl3) δ 7.52-7.53 (m, 2H), 7.28-7.30 (m, 3H), 5.28 (s, 1H), 3.85 (s, 3H), 2.96 (t, J = 7.2 Hz, 2H), 1.24-2.02 (m, 2H), 1.75-1.79 (m, 4H), 1.37-1.42 (m, 6H), 1.04 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 153.9, 147.5, 132.3 (2C), 130.4, 128.8 (2C), 126.5, 122.8, 54.7, 42.9, 34.6, 33.9, 30.8, 27.7, 26.9, 26.3, 24.2, 19.3; LRMS (EI) 382, 213, 169, 125 m/e; HRMS (EI) C19H26O3Se cal’d for 382.10539, found 382.10539.

**Acetic acid 7-methyloctahydroinden-4-(S)-yl ester (62α, major).**

**Acetic acid 7-methyloctahydroinden-4-(R)-yl ester (62β, minor).**

Iodide 53a (1.06 g, 3.13 mmol mmol) was added to a sealed tube equipped with magnetic stir bar and diluted with benzene to 34 mL. AIBN (100 mg, 0.06 mmol) was added to the solution followed by Bu3SnH (0.99 mL, 3.44 mmol) via syringe and placed in a preheated oil bath and allowed to stir at 80°C for 2 h. The reaction was cooled to RT then the benzene was removed in vacuo. Chromatography (100% Hexanes followed by gradient 5-10% Et2O) of the crude mixture gave a 584 mg mixture of inseparable diastereomers (1.5:1) 62α and 62β in 95% combined yield. 62α: 1H NMR (300 MHz, CDCl3) δ 5.00 (dt, J = 10.9, 4.8 Hz, 1H), 1.98 (s, 3H), 1.24-1.86 (m, 12H), 1.03 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 170.6, 72.9, 47.9, 42.8, 41.3, 31.5, 25.7, 24.8, 24.0, 21.3, 20.8, 20.3; IR (neat) 1736.7, 1245.8 cm⁻¹; GC-MS last eluting (M-OAc) 136, 121 m/e. 62β: 1H NMR (300 MHz, CDCl3) δ 4.60 (dt, J = 11.9, 4.8 Hz, 1H), 2.00 (s, 3H), 1.24-
1.86 (m, 12H), 0.98 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.8, 73.9, 49.7, 42.2, 41.4, 36.5, 34.1, 29.2, 28.3, 27.1, 20.7, 19.1; IR (neat) 1736, 1245 cm$^{-1}$; GC-MS first eluting (M-OAc) 136, 121 m/e.

$(cis)$-Carbonic acid methyl ester 7-methyloctahydroinden-4-(S)-yl ester (63$\alpha$, major).

$(cis)$-Carbonic acid methyl ester 7-methyloctahydroinden-4-(R)-yl ester (63$\beta$, minor).

Diastereomers 63$\alpha$ and 63$\beta$ (2:1) were prepared in 68% yield (422 mg) in the same manner as 63$\alpha$ and 63$\beta$ using iodide 53b (723 mg, 2.14 mmol). 63$\alpha$: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.89 (dt, J = 11.0, 5.2 Hz, 1H), 3.77 (s, 3H), 1.26-1.87 (m, 12H), 1.06 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 155.7, 78.4, 54.4, 48.0, 43.1, 41.5, 31.4, 25.7, 24.7, 23.9, 20.8, 20.4; IR (neat) 1747.1 cm$^{-1}$; GC-MS last eluting (M-C$_2$H$_3$O$_3$) 136, 121 m/e. 63$\beta$: $^1$H NMR (300 MHz, CDCl$_3$) 4.80 (m, 1H), 3.76 (s, 3H), 1.26-1.87 (m, 12H), 1.00 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) 155.4, 78.4, 54.4, 49.7, 42.3, 36.5, 33.7, 29.2, 28.3, 27.1, 20.5, 19.0; IR (neat) 1747.1 cm$^{-1}$; GC-MS first eluting (M-C$_2$H$_3$O$_3$) 136, 121 m/e.

**Acetic acid 3-methyl-3-propylcyclohex-1-enyl ester (61a).**

Acetate 61a was made in the same manner as 50 using 1-bromopropane when preparing the Grignard reagent in 68% yield as a yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.06 (s, 1H), 1.98-2.08 (m, 2H), 2.02 (s, 3H), 1.64-1.71 (m, 2H), 1.39-1.46 (m, 2H), 1.15-1.29 (m, 4H), 0.92 (s, 3H), 0.79-0.84 (m, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 169.2, 147.1, 122.9, 45.1, 34.6, 34.0, 27.1, 26.7, 20.9, 19.3, 17.1, 14.7; IR (neat) 1760 cm$^{-1}$; LRMS (EI) (M-CH$_3$) 181 m/e.

**Carbonic acid methyl ester 3-methyl-3-propylcyclohex-1-enyl ester (61b).**

Carbonate 61b was made in the same manner as 51 using 1-bromopropane when preparing the Grignard reagent in 75% yield as a yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.16 (s, 1H), 3.71 (s, 3H), 1.97-2.15 (m, 2H), 1.57-1.84 (m, 2H), 1.36-1.45 (m, 2H),
1.13-1.31 (m, 4H), 0.92 (s, 3H), 0.79-0.83 (m, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 153.9, 147.3, 122.9, 54.5, 45.0, 34.7, 33.9, 26.9, 26.2, 19.2, 17.0, 14.7; IR (neat) 1756 cm$^{-1}$; LRMS (EI) 212 m/e.

(cis)-7-Methyloctahydroinden-4-(S)-ol (64α, major)
(cis)-7-Methyloctahydroinden-4-(R)-ol (64β, minor)

To a 10 mL round bottom flask was added a mixture of 62α,β (0.50 mmol) in dry Et$_2$O (10 mL) and cooled to 0°C under argon. LAH (0.75 mmol) was added portionwise to the solution and allowed to stir for 30 min. The reaction mixture was quenched with H$_2$O (5 mL) and the aqueous layer was extracted with Et$_2$O (3 x 5 mL). The organic layers were combined, dried over MgSO$_4$ and concentrated in vacuo. Chromatography (80:20 Hexanes:EtOAc) gave a 1.5:1 mixture of 64α,β, a clear oil in 50% yield. Data matches literature values. 64α: $^1$H NMR (300 MHz, C$_6$D$_6$) δ 3.68 (dt, $J = 10.6, 4.6$ Hz, 1H), 1.11-1.71 (m, 12H), 0.93 (s, 3H); $^{13}$C NMR (C$_6$D$_6$) δ 69.3, 51.6, 41.1, 31.9, 30.2, 25.0, 23.7, 21.5, 20.7, 18.4; IR (neat) 3340.2 cm$^{-1}$; GC-MS last eluting (M-H) 153, 136, 121 m/e. 64β: $^1$H NMR (300 MHz, C$_6$D$_6$) δ 3.07 (ddd, $J = 17.6, 9.3, 3.9$ Hz, 1H), 1.11-1.71 (m, 12H), 0.90 (s, 3H); $^{13}$C NMR (C$_6$D$_6$) δ 71.1, 54.0, 42.6, 35.7, 34.8, 34.1, 29.3, 27.3, 20.9, 20.1; IR (neat) 3340 cm$^{-1}$; GC-MS first eluting (M-H) minor 153, 136, m/e.

7-Methyloctahydroinden-4-one (54).$^{21}$

To a 1.5:1 mixture of 64α,β (50 mg, 0.32 mmol) in dry DCM (5 mL) was added Dess-Martin periodane (276 mg, 0.8 mmol) and allowed to stir at RT under argon for 1 h. The reaction was diluted with H$_2$O (2 mL) and then extracted with Et$_2$O (3 x 10 mL). The organic layers were combined, dried over MgSO$_4$ and concentrated in vacuo to give 54 in 50% yield. Data matches literature values. $^1$H NMR (300 MHz, C$_6$D$_6$) δ 2.00-2.14 (m, 2H), 1.92-1.98 (m, 2H), 1.53-1.60 (m, 2H), 1.38-1.44 (m, 2H), 1.21-1.26 (m, 2H), 0.8 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 214.0, 60.9, 47.8, 40.4, 39.0, 33.9, 27.4, 27.0, 21.9, 21.4; IR (neat) 1708.3 cm$^{-1}$; LRMS (EI) 151 m/e.
3.1. Procedures for Radical Cyclizations

Stock solutions of iodides 53a,b, selenyl ethers 53c,d and internal standard, \( p \)-dimethoxybenzene, were made in \( C_6D_6 \) and kept under argon and frozen when not in use. Reactions were run in triplicate at each concentration for 53a,c,d. Aliquots from each solution were taken for a \(^1\)H NMR and GC sample before and after the allotted reaction time to determine yields. Gas chromatograms (GC) were run on an Agilent 6850 Series GC System with an HP-1 Methyl Siloxane column (Agilent 19091Z-413E, Capillary 30.0 m x 320 µm x 0.25µm). The initial temperature of the program was 150 °C with a temperature ramp of 5°C/min up to 250 °C a helium flow of 2 mL/min and 8.68 PSI was applied. \( p \)-dimethoxybenzene was used as internal standard and C\(_6\)D\(_6\) or benzene was used as solvent. GC data is reported with a retention time and % area of the total integrated area. GC yields were determined by calculating the response factors (RF) of each compound to the internal standard using:

\[
RF = \frac{\text{mmol standard x area compound}}{\text{mmol compound x area standard}}
\]

Response factors for each compound is as follows:

- 53c: 3.1391  53d: 3.3183  64β (minor), 64α (major): 2.6296  62β (minor), 62α (major): 1.2347  63β (minor), 63α (major): 2.8085
- 53a: 1.4241  53b: 3.0488  54: 1.3677  61a: 1.2691  61b: 3.6176

Retention times for each compound is as follows (min):

- standard: 3.45  54: 4.00  64β (minor), 64α (major): 4.15, 4.04  40: 4.55  62β (minor), 62α (major): 4.93, 4.82  61b: 5.12  63β (minor), 63α (major): 5.48, 5.36  53a: 7.03  53b: 9.40  53c: 9.67  53d: 10.08
3.2. Concentration studies

Aliquots of radical precursors 53a-d (1 equiv) and internal standard, p-dimethoxybenzene (0.1 to 0.2 equiv) were added to sealed tubes equipped with magnetic stir bars and diluted with C\textsubscript{6}D\textsubscript{6} to the proper concentration. AIBN (0.2 equiv) was added to the solutions followed by Bu\textsubscript{3}SnH (1.1 equiv) via syringe and were placed in a preheated oil bath and allowed to stir at 80°C for a predetermined amount of time.

Table 10 Reaction yields of 53c with varying concentrations of Bu\textsubscript{3}SnH

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Table 11 Reaction yields of 53d with varying concentrations of Bu3SnH

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Table 13 Reaction yields of 53b with varying concentrations of Bu₃SnH

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**AIBN Concentration Studies**

Aliquots of iodide 53a (0.124 mmol) and p-dimethoxybenzene (0.05 mmol) were added to sealed tubes equipped with magnetic stir bars and diluted with C₆D₆ to 13.6 mL. AIBN (varying eqs.) was added to each solution followed by Bu₃SnH (0.037 mL, 0.136 mmol) via syringe and were placed in a preheated oil bath and allowed to stir at 80°C for 12 h. AIBN amounts were 0.25 eq (5 mg), 0.5 eq (10 mg), 0.75 eq (15 mg), 1 eq (20 mg), 2 eq (40 mg).

Table 14 Reaction yields of 62α,β with varying concentrations of AIBN

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BIBLIOGRAPHY


See Experimental for the data on all runs, Table 10.

See Experimental for the data on all runs, Table 11.


25 See Experimental for the data on all runs, Table 12.

26 See Experimental for the data on all runs, Table 13.


30 For exact methods and results, see ref. 29.