Zn-Catalyzed Direct Synthesis of
3-Iodo-1,3-dienes from
α-Allenols

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In recent years, chemistry of these compounds has attracted the attention of many chemists giving rise to many studies due to the presence of a cumulated diene in the structure of the compound. Among most important properties of the allenes include:

(1) control of reactivity
(2) control of regioselectivity
(3) transfer of chirality
Iododienes are interesting species for the organic chemistry because of their wide reactivity applications. These compounds are intermediates of many reactions as Diels-Alder reactions, palladium-catalyzed reactions such as Stille, Negishi, and Sonogashira and carbonylation cross-couplings, and solvolysis reactions and metatation.
Okamoto et al. described the oxidant addition of \((\eta^2\text{-propene})\text{Ti}(O\text{-i-Pr})_2\) to \(\alpha\text{-allenyl carbonates}\) to form titanium compounds that by reacting them with molecular iodine they obtained 2-iodo-1,3-dienes.

Nishimaya et al. observed the obtaining of 2-iodo-1,3-butadiene by treatment of 1-trimethylsilyl-2,3-butadiene with \(I_2\) and tetra-n-butylammonium fluoride (TBAF).
The main aim of this project is the development of a new synthetic method that allows to obtain 3-iodo-1,3-dienes directly from α-allenols through a sustainable process.
Allenol 1a was selected as model substrate. Initial experiments were performed though the reaction of 1a with ZnI₂ and p-toluenesulfonic acid monohydrate in dichloromethane which provided the 3-iodo-1,3-diene 2a as the only reaction product.

\[
\begin{align*}
\text{Me} & \quad \text{OH} \\
\text{Me} & \quad \text{+=} \\
\text{1a (1 equiv.)} & \quad 0.025 \text{ equiv.} & \quad 0.025 \text{ equiv.} & \quad \text{2a (2\%)} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>ZnI₂ (equiv.)</th>
<th>TsOH·H₂O (equiv.)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.025</td>
<td>0.025</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.1</td>
<td>33</td>
</tr>
<tr>
<td>3</td>
<td>1.2</td>
<td>0.1</td>
<td>37</td>
</tr>
<tr>
<td>4</td>
<td>1.2</td>
<td>-</td>
<td>48</td>
</tr>
</tbody>
</table>

The yield was very low and the reaction was optimized conditions were optimized (see Table). The highest yield of the product was achieved by employing 1.2 equiv. of ZnI₂ at room temperature in dichloromethane without the presence of p-toluenesulfonic acid.
The scope of the reaction was explored in different α-allenols giving rise to the corresponding 3-iodo-1,3-dienes 2a-h in reasonable yields (22–69%) and good (E)-diastereoselectivity.
Results and Discussion

Possible pathway for the generation of 3-iodo-1,3-dienes 2 from α-allenols 1.
In conclusion, we present here the regiocontrolled synthesis of 3-iodo-1,3-dienes, directly from $\alpha$-allenols through a sustainable process using zinc (II) derivatives as metallic promoter.
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