CHAPTER IV

IODINE-CATALYZED ONE-POT THREE-COMPONENT SYNTHESIS OF HOMOALLYL BENZYL ETHERS
4.1. INTRODUCTION

The allylation of acetal using allytrimethylsilane has attracted much attention as a useful method to generate homoallyl ethers and homoallyl acetates. Homoallyl ethers and homoallyl acetates are versatile functional groups amenable to further synthetic manipulation. Homoallyl ethers can serve as useful precursors to cyclic enol ethers via ring closing metathesis reactions. Cyclic enol ethers play a vital role in the synthesis of bioactive compounds such as glycols, polyether antibiotics and natural products and nucleoside antibiotics. Optically active homoallyl alcohols can also be synthesized from chiral homoallyl ethers via open-chain acetal derivatives.
4.2. REVIEW OF LITERATURE

Synthesis of homoallyl ether from aldehydes is an important carbon-carbon bond formation reaction. Homoallyl ethers can also be synthesized by allylation of acetals with allylsilanes. These reactions were promoted by a variety of Lewis acids. Sakurai and co-workers\textsuperscript{11} synthesized homoallyl ethers from various acetals including aliphatic, alicyclic and aromatic acetals by reaction with allyltrimethylsilane in presence of stoichiometric amount of TiCl\textsubscript{4} at a temperature of -78 °C under nitrogen atmosphere (Scheme 4.1)

\[ \text{Scheme 4.1} \]

However, the reaction of allyltrimethylsilane with ethyl orthoformate gave a diallylated product (Scheme 4.2).

\[ \text{Scheme 4.2} \]

With α,β-unsaturated acetals also, the reaction gave only the diallylated products. This reaction gave the expected monoallylated products when Lewis acids like AlCl\textsubscript{3} and BF\textsubscript{3}.Et\textsubscript{2}O\textsuperscript{12} were used. These Lewis acids are relatively toxic and their use in stoichiometric amount in these reactions is the drawback of these reactions. Later on, various Lewis acids like trimethylsilyl triflate (TMSOTf),\textsuperscript{13} iodotrimethylsilane,\textsuperscript{14} trityl perchlorate\textsuperscript{15}
and Ph$_2$BOTf$^{15}$ were used as efficient catalysts for allylation of acetals. In all cases, the corresponding homoallyl ethers were obtained in good yields. However, these catalysts were found ineffective for allylation of orthoesters except trimethylorthoformate. Sakurai et al.$^{16}$ reported that in the allylation reaction of allylsilane with $\alpha$-chloro ethers, iodotrimethylsilane and TMSOTf (5-10 mol%) activated the C-Cl bond of $\alpha$-chloro ethers selectively and catalyzed the reaction to afford the corresponding homoallyl ethers (Scheme 4.3).

![Scheme 4.3](image)

Sakurai$^{17}$ also found that the reaction of crotylsilane with aliphatic acetals activated by Lewis acids like TiCl$_4$, BF$_3$.Et$_2$O, iodotrimethylsilane, trimethylsilyl triflate proceeded smoothly in a syn selective mode while the same reaction with aromatic acetals was dependent on the geometry of the crotylsilane used (Scheme 4.4).

![Scheme 4.4](image)

Solid acids could catalyze the allylation of acetals and afforded the corresponding homoallyl ethers in excellent yields.$^{18}$ Hollis et al.$^{19}$ used a titanium based catalyst, [TiCp$_2$(CF$_3$SO$_3$)$_2$] for the allylation reactions of
acetals and ketals and found that the catalyst was effective for those reactions. Orthoesters were also allylated by using this catalyst. Later, Trehan and co-workers\(^20\) reported a trimethylsilyl bis(fluorosulfonyl)imide catalyzed allylation reaction of acetals and found that trimethylsilyl bis(fluorosulfonyl)imide show better catalytic activity than that of trimethylsilyl triflate. Suzuki \textit{et al}.\(^21\) reported a BiBr\(_3\) catalyzed allylation of acetals at room temperature and found similar catalytic efficiency with that of trityl perchlorate and Ph\(_2\)BOTf in the allylation reaction. A catalytic amount of bismuth triflate was also found effective for allylation of acetal\(^22\) Zerth \textit{et al}.\(^23\) reported an efficient TMSOTf catalyzed protocol for allylation of acetals in ionic liquids (Scheme 4.5). The corresponding homoallyl ethers were obtained in good yields.

\[
\begin{align*}
\text{R-} & \text{OR'} + \text{SiMe}_3 & \xrightarrow{\text{TMSOTf (5-20 mol\%)} / [bmm][PF6] or [bmm][OTf], r.t} & \text{R-} \text{OR'} \\
\end{align*}
\]

\textbf{Scheme 4.5}

Jung and Maderna\(^24\) synthesized homoallyl ether from various acetals (aromatic, aliphatic and cyclic) and allyltrimethylsilane by using aluminium bromide as catalyst in the presence of triethyl aluminium as a desicant. They found that addition of a catalytic amount of copper bromide (CuBr) could improve the yield of the homoallyl ether. They also carried out the reaction under microwave heating and using CuBr as a promoter.\(^25\) This method worked well for aromatic acetals having no electron-withdrawing group.
Homoallyl ethers could be synthesized directly from aldehydes in one-pot in presence of a catalytic amount of iodo(trimethyl)silane (Scheme 4.6)\textsuperscript{26}

\[
\begin{array}{c}
R' \equiv O + R'OSiMe_3 + \text{SiMe}_3 \quad \text{TMSi (10 mol\%)} \quad \text{CH}_2Cl_2, r t \quad \text{R} \quad \text{OR}' \\
\end{array}
\]

Scheme 4.6

Seeback\textsuperscript{27} developed another variation for synthesis of homoallyl ethers. The reaction was carried out by treating an aldehyde with dialkoxy-dichlorotitanium and allyl(trimethyl)silane at -75 °C (Scheme 4.7)

\[
\begin{array}{c}
\text{RCHO} + \quad \text{Cl}_2\text{Ti(OR')}_2 \quad \text{75 °C} \quad \text{R} \quad \text{OR'} \\
\end{array}
\]

Scheme 4.7

Later on, a trimethylsilyl triflate (TMSOTf)\textsuperscript{28} catalyzed method was reported for synthesis of homoallyl ether directly from carbonyl compounds (Scheme 4.8).

\[
\begin{array}{c}
\text{R} \quad \text{OR'} \\
\end{array}
\]

Scheme 4.8

A ferric chloride catalyzed method was also reported for synthesis of homoallyl ethers from aldehydes\textsuperscript{29} Mohan \textit{et al.}\textsuperscript{30} reported another method for synthesis of homoallyl ethers from aldehydes in presence of catalytic amount of bismuth (III) triflate.
4.3. PRESENT WORK

OBJECTIVE

Allylation of acetals using allyltrimethylsilane is a useful method for synthesis of homoallyl ethers. Although there are several reports on this allylation reaction, these methods associated with several drawbacks (1) Many acetals are not commercially available and must be synthesized from their corresponding aldehydes (2) Most of the methods only report allylation of dimethyl or diethyl acetals that results in the formation of homoallyl methyl or ethyl ethers and further synthetic manipulation of the ethers is not practicable due to inactivity of the aliphatic ether linkage. (3) Many of these methods use corrosive and moisture sensitive catalysts such as TMS triflate. As benzyl ethers are preferred to their alkyl counterparts due to easy deprotection of the benzyl group, synthesis of homoallyl benzyl ethers has received scant attention in the literature. There are only a few reports in the literature for synthesis of homoallyl benzyl ether. As a continuation of our work on iodine catalyzed reaction, we would like to examine the efficiency of iodine catalyst for synthesis of homoallyl benzyl ether from aldehydes (Scheme 4.9).

\[
\text{Scheme 4.9}
\]
4.4. RESULTS AND DISCUSSION

The allylation reaction was carried out under various conditions taking benzaldehyde as a model substrate. Initially, allyltrimethylsilane (1.2 mmol) was added to a solution of benzaldehyde (1 mmol), benzyloxytrimethylsilane (1.2 mmol) and iodine (10 mol%) in acetonitrile at room temperature. After 24 hour of reaction at room temperature, the reaction afforded 60% yield of the corresponding homoallyl benzyl ether. Then a screening was carried out on various parameters like solvents, catalyst concentration and the amount of the benzyloxytrimethylsilane and allyltrimethylsilane. Dichloromethane was found to be the best among the solvents studied for this reaction (Table 4.1, entry 2).

Table 4.1: Synthesis of homoallyl benzyl ether in different solvents

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (%)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_3$CN</td>
<td>24</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>CH$_2$Cl$_2$</td>
<td>24</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td>CH$_3$OH</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Diethyl ether</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>CH$_3$NO$_2$</td>
<td>24</td>
<td>43</td>
</tr>
<tr>
<td>6</td>
<td>DMF</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>THF</td>
<td>24</td>
<td>0</td>
</tr>
</tbody>
</table>

*aisolated yield after chromatographic purification*
The reaction was then examined under different concentrations of the catalyst and also with different concentrations of benzyloxytrimethylsilane and allyltrimethylsilane (Table 4.2). Use of 10 mol% iodine gave the best result but the yield was not satisfactory. The reaction was then studied by lowering the temperature to 0 °C. Surprisingly, the reaction completed in 45 minutes giving 86% yield of the product. So, the molar ratio of benzaldehyde, benzyloxytrimethylsilane, allyltrimethylsilane and iodine was 1:1.2:1.2:0.1 in dichloromethane at 0 °C (Table 4.2, entry 6)

Table 4.2: Synthesis of homoallyl benzyl ether in dichloromethane

<table>
<thead>
<tr>
<th>Entry</th>
<th>Benzaldehyde (mmol)</th>
<th>Benzyloxytrimethylsilane (mmol)</th>
<th>Allyltrimethylsilane (mmol)</th>
<th>Iodine (mol%)</th>
<th>Temp (°C)</th>
<th>Time (min)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.2</td>
<td>1.2</td>
<td>10</td>
<td>27</td>
<td>210</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1.2</td>
<td>1.2</td>
<td>20</td>
<td>27</td>
<td>120</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1.2</td>
<td>1.2</td>
<td>5</td>
<td>27</td>
<td>300</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1.1</td>
<td>1.2</td>
<td>10</td>
<td>27</td>
<td>210</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>1.1</td>
<td>1.2</td>
<td>10</td>
<td>0</td>
<td>40</td>
<td>82</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>1.2</td>
<td>1.2</td>
<td>10</td>
<td>0</td>
<td>45</td>
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<tr>
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<td>1.5</td>
<td>10</td>
<td>0</td>
<td>30</td>
<td>75</td>
</tr>
</tbody>
</table>

*isolated yield after chromatographic purification

The scope of the reaction was then examined using various aldehydes. The results were shown in Table 4.3.
Table 4.3: Synthesis of homoallyl benzyl ethers using iodine as catalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde</th>
<th>Time (min)</th>
<th>Homoallyl benzyl ether</th>
<th>Yield(^a) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{C}_6\text{H}_5\text{CHO})</td>
<td>45</td>
<td>(\text{OCH}_2\text{Ph})</td>
<td>86</td>
</tr>
<tr>
<td>2</td>
<td>(\text{Br}\text{C}_6\text{H}_4\text{CHO})</td>
<td>45</td>
<td>(\text{OCH}_2\text{Ph})</td>
<td>76</td>
</tr>
<tr>
<td>3</td>
<td>(\text{F}\text{C}_6\text{H}_4\text{CHO})</td>
<td>60</td>
<td>(\text{OCH}_2\text{Ph})</td>
<td>74</td>
</tr>
<tr>
<td>4</td>
<td>(\text{Cl}\text{C}_6\text{H}_4\text{CHO})</td>
<td>60</td>
<td>(\text{OCH}_2\text{Ph})</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>(\text{Cl}\text{C}_6\text{H}_4\text{CHO})</td>
<td>45</td>
<td>(\text{OCH}_2\text{Ph})</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>(\text{Cl}\text{C}_6\text{H}_4\text{CHO})</td>
<td>45</td>
<td>(\text{OCH}_2\text{Ph})</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>(\text{MeO}\text{C}_6\text{H}_4\text{CHO})</td>
<td>40</td>
<td>(\text{OCH}_2\text{Ph})</td>
<td>76</td>
</tr>
<tr>
<td>8</td>
<td>(\text{O}_2\text{N}\text{C}_6\text{H}_4\text{CHO})</td>
<td>45</td>
<td>(\text{OCH}_2\text{Ph})</td>
<td>77</td>
</tr>
<tr>
<td>9</td>
<td>(\text{C}_6\text{H}_4\text{CHO})</td>
<td>40</td>
<td>(\text{OCH}_2\text{Ph})</td>
<td>82</td>
</tr>
<tr>
<td>10</td>
<td>(\text{NCH}_2\text{CH}_2\text{CHO})</td>
<td>90</td>
<td>(\text{OCH}_2\text{Ph})</td>
<td>65</td>
</tr>
</tbody>
</table>

\(^a\) isolated yield after chromatographic purification
From Table 4.3, it can be concluded that aromatic substrates bearing functional groups such as -CH₃, -OCH₃, -Cl, -Br, -NO₂ and -F all reacted smoothly to give the corresponding homoallyl benzyl ethers in high yields. The reaction also works with aliphatic aldehyde such as cinnamaldehyde but a very low yield was found.

The products are characterized by IR and NMR spectroscopy. In the IR spectrum of 4-benzyloxy-4-phenyl butene-1, bands at 1266 cm⁻¹ and 1089 cm⁻¹ indicate the presence of CH₂-O-CH₂ group. Bands at 1666 cm⁻¹ and 1636 cm⁻¹ are due to C=C stretching. In ¹H NMR spectra, the CH proton attached to the oxygen atom appears as a triplet at δ = 4.25 ppm. A multiplet signal at δ = 7.27-7.1 ppm arises due to ten aromatic protons. Benzylic protons are observed as a multiplet at δ = 4.95-4.88 ppm. The CH proton of the olefinic double bond appear as a multiplet at δ = 5.73-5.62 ppm while the CH₂ protons appear as two doublets at δ = 4.35 and 4.15 ppm. The multiplet signals at δ = 2.56-2.48 and 2.35-2.29 ppm are due to the CH₂ protons attached to the olefinic bond.

![Figure 4.1: ¹H NMR spectra of 4-benzyloxy-4-phenyl butene-1](image-url)
The mass spectra of the compound shows prominent peaks at m/z value 197, 91, 77, 65 and 41. The peak at m/z = 197 is due to [PhCH₂OCHPh]⁺. The base peak at m/z = 91 is due to the tropylium ion [C₇H₇]⁺. The peaks at m/z = 77, 65 and 41 are due to [C₆H₅]⁺, [C₅H₅]⁺ and [C₃H₅]⁺ ions respectively.

Figure 4.2: Mass spectra of 4-benzyloxy-4-phenyl butene-1

In case of 4-benzyloxy-4-(4-fluoro-phenyl)-butene-1, the IR spectra give signals at 1661 cm⁻¹ which is responsible for C=C stretching. Bands at 1263 cm⁻¹ and 1087 cm⁻¹ are due to C-O-C stretching. The fluoro group attached to the aromatic ring is ascertained by a signal at 1224 cm⁻¹. In the ¹H NMR spectra, the CH proton attached to oxygen appears as a triplet at δ = 4.23 ppm. Signals at δ = 7.23-7.11 ppm (multiplet) and 6.93 ppm (doublet) arises due to the nine aromatic protons. A multiplet is observed at δ = 4.93-4.89 ppm which is due to benzylic protons. The olefinic CH proton appear as a multiplet at δ = 5.69-5.59 ppm while doublet signals are observed at δ = 4.32 and 4.14 ppm which are due to CH₂ group of the olefinic double bond. The multiplet signals at δ = 2.51-2.44 and 2.31-2.24 ppm are due to the two protons CH₂ group attached to the double bond.
For the compound 4-benzyloxy-4-(4-tolyl)-butene-1, the IR spectra give signals at 1272 and 1075 cm^{-1} indicating the presence of C-O-C group. In the $^1$H NMR spectra, a triplet signal is observed at $\delta = 4.24$ ppm which is due to the CH proton attached to the oxygen atom. A multiplet signal at $\delta = 7.27-7.05$ ppm arises due to nine aromatic protons. The benzylic CH$_2$ protons appear as a multiplet signal at $\delta = 4.97-4.91$ ppm. A multiplet signal observed at $\delta = 5.75-5.65$ ppm is due to the CH proton of the double bond while two doublet signals are observed at $\delta = 4.37$ and 4.16 ppm which are due to the two protons of the CH$_2$ group of the double bond. The multiplet signals at $\delta = 2.58-2.50$ and 2.36-2.33 ppm are due to the two protons of the -CH$_2$-CH=CH$_2$ group. The CH$_3$ protons attached to the aromatic ring are observed as singlet at $\delta = 2.27$ ppm.
In the IR spectrum of 4-benzyloxy-4-(4-nitrophenyl)-butene-1, two bands at 1269 cm$^{-1}$ and 1097 cm$^{-1}$ is due to C-O-C stretching. Signals at 1666 and 1641 cm$^{-1}$ are indicative of C=C stretching. The $^1$H NMR spectra shows a triplet signal at $\delta = 4.21$ ppm for the CH proton attached to the oxygen atom. The nine aromatic protons give three signals at $\delta = 8.10$ ppm (doublet), 7.37 ppm (doublet) and 7.25-7.13 ppm (multiplet). The two protons of the -OCH$_2$Ph group appear as multiplet signal at $\delta = 4.93$-$4.88$ ppm. The CH proton and CH$_2$ proton of the double bond appear as two multiplets at $\delta = 5.72$-$5.58$ and 4.39-4.34 ppm respectively. The multiplet signals at $\delta = 2.54$-$2.46$ and 2.38-2.29 ppm are due to the two protons of the -CH$_2$-CH=CH$_2$ group.
4.5. PROBABLE MECHANISM

A probable mechanistic pathway to explain the allylation process is depicted in Scheme 4.10. The reaction proceeds via the formation of acetal. The acetal was generated in situ by the reaction of aldehydes with benzyloxytrimethylsilane and converted into the corresponding homoallyl benzyl ether by the reaction of allyltrimethylsilane.

\[
\begin{align*}
\text{RCHO} + \text{PhOSiMe}_3 \rightarrow \text{ROCH}_2\text{Ph} \\
\text{A} \\
\text{I}_2 \rightarrow \text{PhOSiMe}_3 \\
\text{B}
\end{align*}
\]

Scheme 4.10
4.6. CONCLUSION

Synthesis of homoallyl benzyl ether from aldehydes in the presence of catalytic amount of iodine is found to be effective. The reaction occurs at room temperature as well as at 0 °C. Yields are found better at 0 °C. Moreover, the reaction is faster at low temperature. The procedure is applicable to both aromatic and aliphatic aldehydes but yield is better for aromatic aldehydes.

4.7. EXPERIMENTAL SECTION

(A) Preparation of Benzyloxytrimethyl Silane

At room temperature, to a solution of potassium iodide (1.66 gm) in N, N-dimethyl foramide (10 ml), petroleum ether (3.75 ml), triethyl amine (4.2 ml), benzyl alcohol (2.6 ml), chlorotrimethylsilane (3.3 ml) were added. The round bottom flask was sealed immediately by capping plug. The mixture was then shaked for 5-10 minutes and was kept at room temperature for 10 hour. The petroleum ether layer was separated out from the DMF layer. The DMF layer was washed with cold petroleum ether 2-3 times. Petroleum ether layers were combined and washed rapidly with cold saturated sodium chloride, dried over anhydrous sodium sulfate and concentrated to get the pure product. About 90 % yield of the product was obtained.
(B) General Procedure for synthesis of Homoallyl Benzyl ether

To a solution of iodine (10 mol%) in dichloromethane (1 ml), aldehyde (1 mmol), benzyloxytrimethylsilane (1.2 mmol) and allyltrimethylsilane (1.2 mmol) were added successively at 0 °C. The mixture was then stirred at 0 °C for appropriate time. After completion of the reaction, sodium thiosulfate was added. Then water was added and the reaction was stirred for 20 minutes. It was then extracted with ethylacetate, washed with brine, dried over sodium sulfate and concentrated. The crude product was purified by column chromatography over silica gel (60-120 mesh) with ethylacetate-petroleum ether (5 %) as eluent.

(C) Experimental Data

Benzyloxytrimethyl silane

Yield: 90%

IR (neat, cm⁻¹): 3030, 2957, 1469, 1454, 1377, 1250, 1207, 1096, 1069, 1027, 874, 728

¹H NMR (400 MHz, CDCl₃): 7.34-7.25 (m, 5 H), 4.70 (s, 2H), 0.16 (s, 9H)
(1) 4-Benzylxy-4-phenyl butene-1

**Yield:** 86%

**IR (neat, cm\(^{-1}\)):** 3058, 3029, 2921, 2852, 1666, 1636, 1602, 1489, 1445, 1266, 1089, 1023, 915

\(^1\)H NMR (400 MHz, CDCl\(_3\)): 7.27-7.1 (m, 10H), 5.73-5.62 (m, 1H), 4.95-4.88 (m, 2H), 4.35 (d, \(J = 12\) Hz, 1H), 4.25 (t, \(J = 6.8\) Hz, 1H), 4.15 (d, \(J = 12\) Hz, 1H), 2.56-2.48 (m, 1H), 2.35-2.29 (m, 1H)

**Mass (m/z, % rel. intensity):** 197 (10), 141 (22), 91 (100), 77 (6), 65 (6), 41 (8)

(2) 4-Benzylxy-4-(4-bromo-phenyl)-butene-1

**Yield:** 76%

**IR (neat, cm\(^{-1}\)):** 3078, 3029, 2921, 2852, 1636, 1593, 1486, 1450, 1259, 1073, 1008, 915, 823

\(^1\)H NMR (400 MHz, CDCl\(_3\)): 7.46 (d, \(J = 8.0\) Hz, 2H), 7.34-7.23 (m, 5H), 7.18 (d, \(J = 8.4\) Hz, 2H), 5.78-5.68 (m, 1H), 5 03-4 98 (m, 2H), 4 42 (d, \(J = 12\)Hz, 1H), 4.30 (t, \(J = 6.8\) Hz, 1H), 4.24(d, \(J = 12\) Hz, 1H), 2.59-2.54 (m, 1H), 2.41-2.34 (m, 1H)

(3) 4-Benzylxy-4-(4-fluro-phenyl)-butene-1

**Yield:** 74%

**IR (neat, cm\(^{-1}\)):** 2921, 2852, 1661, 1602, 1440, 1381, 1263, 1224, 1087, 1032, 832
\textbf{1H NMR (400 MHz, CDCl\textsubscript{3})}: 7.23-7.11 (m, 7H), 6.93 (t, \(J = 8.8\) Hz, 2H), 5.69-5.59 (m, 1H), 4.93-4.89 (m, 2H), 4.32 (d, \(J = 12\) Hz, 1H), 4.23 (t, \(J = 6.8\) Hz, 1H), 4.14 (d, \(J = 12\) Hz, 1H), 2.51-2.44 (m, 1H), 2.31-2.24 (m, 1H)

\textbf{(4) 4-Benzyl oxy-4-(4-chloro-phenyl)-butene-1}

\textbf{Yield:} 78\%

\textbf{IR (neat, cm\textsuperscript{-1})}: 3068, 3029, 2921, 2862, 1666, 1631, 1598, 1533, 1489, 1450, 1268, 1088, 1018, 822

\textbf{1H NMR (400 MHz, CDCl\textsubscript{3})}: 7.22-7.08 (m, 9H), 5.68-5.58 (m, 1H), 4.92-4.88 (m, 2H), 4.32 (d, \(J = 12\) Hz, 1H), 4.21 (t, \(J = 6.8\) Hz, 1H), 4.13 (d, \(J = 11.6\) Hz, 1H), 2.51-2.44 (m, 1H), 2.31-2.24 (m, 1H)

\textbf{(5) 4-Benzyl oxy-4-(2-chloro-phenyl)-butene-1}

\textbf{Yield:} 85\%

\textbf{IR (neat, cm\textsuperscript{-1})}: 3068, 3019, 2921, 2852, 1636, 1598, 1523, 1443, 1263, 1090, 1033

\textbf{1H NMR (400 MHz, CDCl\textsubscript{3})}: 7.61-7.08 (m, 9H), 5.98-5.87 (m, 1H), 5.13-5.07 (m, 2H), 4.97 (t, \(J = 6.4\) Hz, 1H), 4.50 (d, \(J = 11.6\) Hz, 1H), 4.35 (d, \(J = 12\) Hz, 1H), 2.55 (t, \(J = 6.4\) Hz, 2H)

\textbf{(6) 4-Benzyl oxy-4-(3-chloro-phenyl)-butene-1}

\textbf{Yield:} 80\%

\textbf{IR (neat, cm\textsuperscript{-1})}: 3068, 3029, 2921, 2852, 1666, 1636, 1592, 1450, 1430, 1263, 1077, 1028, 783

178
$^1$H NMR (400 MHz, CDCl$_3$): 7.25-7.08 (m, 9H), 5.7-5.6 (m, 1H), 4.97-4.90 (m, 2H), 4.36 (d, $J = 12$ Hz, 1H), 4.22 (t, $J = 6.4$ Hz, 1H), 4.16 (d, $J = 12$ Hz, 1H), 2.52-2.45 (m, 1H), 2.33-2.26 (m, 1H)

(7) 4-Benzyl oxy-4-(4-tolyi)-butene-1

Yield: 76%

IR (neat, cm$^{-1}$): 3027, 2921, 2853, 1609, 1499, 1446, 1272, 1075, 1027.

$^1$H NMR (400 MHz, CDCl$_3$): 7.27-7.05 (m, 9H), 5.75-5.65 (m, 1H), 4.97-4.91 (m, 2H), 4.37 (d, $J = 11.6$ Hz, 1H), 4.24 (t, $J = 7.2$ Hz, 1H), 4.16 (d, $J = 12$ Hz, 1H), 2.58-2.50 (m, 1H), 2.36-2.33 (m, 1H), 2.27 (s, 3H)

(8) 4-Benzyl oxy-4-(4-methoxy-phenyl)-butene-1

Yield: 77%

IR (neat, cm$^{-1}$): 3038, 2931, 2860, 1632, 1604, 1485, 1440, 1260, 1064, 1021.

$^1$H NMR (400 MHz, CDCl$_3$): 7.22-7.09 (m, 7H), 6.75 (d, $J = 8.8$ Hz, 2H), 5.67-5.55 (m, 1H), 4.90-4.83 (m, 2H), 4.28 (d, $J = 12$ Hz, 1H), 4.16 (t, $J = 6.8$ Hz, 1H), 4.09 (d, $J = 12$ Hz, 1H), 3.66 (s, 3H), 2.51-2.44 (m, 1H), 2.29-2.23 (m, 1H)

(9) 4-Benzyl oxy-4-(4-nitro-phenyl)-butene-1

Yield: 82%

IR (neat, cm$^{-1}$): 3068, 3029, 2921, 2862, 1666, 1641, 1605, 1524, 1494, 1454, 1269, 1097, 1046, 1023, 854
\[ ^1H\text{NMR (400 MHz, CDCl}_3\]): 8.10 (d, J = 9.2 Hz, 2H), 7.37 (d, J = 11.2 Hz, 2H), 7.25-7.13 (m, 5H), 5.72-5.58 (m, 1H), 4.93-4.88 (m, 2H), 4.39-4.34 (m, 2H), 4.21 (d, J = 11.6 Hz, 1H), 2.54-2.46 (m, 1H), 2.36-2.29 (m, 1H) \]

(10) 4-Benzyloxy-6-phenyl-1,5-hexadiene

Yield: 65%

\[ ^1H\text{NMR (400 MHz, CDCl}_3\]): 7.38-7.20 (m, 10H), 6.86 (d, J = 7.6 Hz, 1H), 6.10 (dd, J = 8 Hz, J = 16 Hz, 1H), 5.88-5.68 (m, 1H), 5.04-4.95 (m, 2H), 4.38 (d, J = 12 Hz, 1H), 4.26 (t, J = 7.2 Hz, 1H), 4.21 (d, J = 12 Hz, 1H), 2.65-2.55 (m, 1H), 2.52-2.42 (m, 1H) \]

\[ \text{IR (neat, cm}^{-1}\): 2931, 2819, 1494, 1448, 1359, 1099, 968, 915, 749, 693 \]
4.8. REFERENCES


