CHAPTER VI

Studies Directed Towards the Bromination of Cyclic Vinylsilanes: Effect of Ring Size
Introduction

It was discussed in Chapter IV that electrophilic substitution reactions of vinylsilanes are some of the most widely studied reactions in organosilicon chemistry. One of the reactions of vinylsilanes is the electrophilic substitution with halogen electrophiles to yield vinylhalides.\textsuperscript{48} Thus, vinylsilanes are used as precursors for the synthesis of vinylhalides and vice versa. The regio-specific substitution is due to the $\beta$-silyl effect.\textsuperscript{61-65} The stereochemistry of the products depends on the reaction conditions, nature of halogenating agent and substituents on the vinylsilane moiety.\textsuperscript{164,165}

The electrophilic bromination of vinylsilanes has so far been restricted mainly to substituted linear vinylsilanes using molecular bromine as the brominating agent at low temperatures. The bromination reaction of simple cyclic vinylsilanes has been less studied.

In stark contrast to electrophilic substitution reactions of vinylsilanes, the addition reactions to vinylsilanes is less studied. To our knowledge there is only one report which describes the addition reaction of molecular bromine to 1-trimethylsilylcyclohexene to form 1,2-dibromo-1-trimethylsilylcyclohexane (Scheme VI. 1).\textsuperscript{268}

![Scheme VI. 1](image)

There are no other reports which study the addition of halogens to cyclic vinylsilanes or studies which are directed towards the effect of ring size or ring strain on the product distribution of the bromination of cyclic vinylsilanes.
Earlier during the course of our studies, our laboratory had reported the use of NBS-Et$_3$N for the preparation of $\alpha$-bromo-$\alpha,\beta$-unsaturated carbonyl compounds. The novel cyclic bromides were ultimately converted to novel $\alpha$-trimethylsilyl cyclic enones.$^{269}$

Among several known brominating agents, one of the reagents documented in the literature is copper (II) bromide in a range of solvents.$^{270}$ The reaction of cupric (II) bromide with alkenes is known to yield 1,2-dibromoalkanes as addition products (Scheme VI. 2).$^{270b}$

\[
\text{alkene} + 2\text{CuX}_2 \rightarrow \text{alkene-Br}_2 + 2\text{CuX}
\]

**Scheme VI. 2**

The use of CuBr$_2$ in the bromination of vinylsilanes is limited. Kumada reported the conversion of alkenyl pentafluorosilicates to alkenyl bromides using CuBr$_2$ with retention of configuration (Scheme VI. 3)$^{271}$

\[
\text{R} \equiv \text{SiF}_5^{2-} \underset{\text{CuBr}_2}{\xrightarrow{}^{\cdot}} \text{R} \equiv \text{Br}
\]

**Scheme VI. 3**

Babudri showed the conversion of linear aliphatic vinylsilanes to the corresponding alkenyl bromides with both retention and inversion of the configuration of the double bond (Scheme VI. 4)$^{272}$

\[
\text{R} \equiv \text{SiMe}_3 \underset{\text{CuX}_2/\text{LiBr}}{\xrightarrow{}^{\cdot}} \text{R} \equiv \text{Br} + \text{R} \equiv \text{Br}^\prime
\]

**Scheme VI. 4**
In this Chapter, we now wish to report the novel bromination reaction studies of simple cyclic vinylsilanes 67-71 with Cu Br₂/CH₃CN. The direct bromination with molecular bromine in CH₂Cl₂ was used as control.

*Present work:*

The cyclic vinylsilanes 67-71 were prepared by established procedures. Magnetic stirring of 15 mmol of cyclic vinylsilane and 30 mmol of CuBr₂ in 30 mL acetonitrile solvent developed a deep olive-green coloration. All reactions were continuously monitored by GC. The reaction of 1-trimethylsilylcyclopentene 67, 1-trimethylsilylcyclohexene 68 and 1-trimethylsilylcycloheptene 69 furnished the corresponding 1,2-dibromo-adducts with the retention of the silyl-group yielding 1,2-dibromo-1-trimethylsilylcyclopentane 72, 1,2-dibromo-1-trimethylsilylcyclohexane 73 and 1,2-dibromo-1-trimethylsilylcycloheptane 74 respectively.

However, in case of 1-trimethylsilylcyclooctene 70 and 1-trimethylsilylcyclododecene 71, the bromo-desilylated products 1-bromocyclooctene 75 and 1-bromocyclododecene 76 respectively along with minor amounts of other isomers which we suspect to be the transannular bromodesilylated products as indicated by GC-MS were formed. The formation of 75 and 76 were confirmed by the GC-MS analysis of the authenticated samples. Distillation under reduced prepssure gave the 1-bromocycloalkenes 75 in 50-53% yield and 76 in 46-49% yield. Earlier work by Nagendrappa has indicated that the ratio of trans:cis isomers of 71 to be 3:2 respectively. We also propose, based on GC-MS analysis, the ratio of trans:cis isomers of 76 to be approximately 60:40 (*Scheme V1.5*).
The direct addition of molecular bromine in CH₂Cl₂ to cyclic vinylsilanes 67 - 71 as control and standard was also carried out. These reactions too proceeded as in the case of copper (II) bromide reactions, giving identical products. All reactions were carried out for a minimum of five experiments. The yields of the products are given in Table VI. 1.
Table VI. 1. Bromination of Cyclic vinylsilanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Product</th>
<th>Yield</th>
<th>Br₂</th>
<th>Bp °C / 1mm</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu Br₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>73-76</td>
<td>77-79</td>
<td>65 – 67</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>72</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>75-78</td>
<td>79-82</td>
<td>73 - 76</td>
<td>268</td>
</tr>
<tr>
<td>68</td>
<td>73</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>83-85</td>
<td>83-87</td>
<td>86 – 89</td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>74</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>50-53</td>
<td>51-54</td>
<td>53-55</td>
<td>214</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lit. (54–56°C/1mm)</td>
</tr>
<tr>
<td>70</td>
<td>75</td>
<td></td>
<td></td>
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<tr>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td>46-49</td>
<td>48-53</td>
<td>112-114</td>
<td>214</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lit. (92–95°C/0.6mm)</td>
</tr>
</tbody>
</table>

The bromoproducts were isolated after distillation under reduced pressure 72 – 76.
In the case of the dibromoadducts 72-74, the compounds were isolated exclusively. Even at their boiling points at 1 mm Hg pressure, no elimination products were observed. The isolation of pure distilled products 72-74 in our laboratory conditions indicates the high stability of the dibromoadducts at ambient temperature. The product distribution of both the brominating agents copper bromide and molecular bromine clearly indicate the role of ring size upon the addition over electrophilic substitution reactions.

**Mechanism:**

The mechanism for formation of products using molecular bromine is expected to go through the conventional three-membered bromonium ion intermediate.\textsuperscript{274} In the cyclic vinylsilanes 67-69, trans-attack by bromide ion leads to the formation of 72-74. Due to ring size constraints, anti-elimination of bromotrimethylsilane is disallowed. However in the eight- and twelve- membered rings due to flexibility of the rings overall electrophillic substitution occurs at the ipso position to form products 75, 76 via β- silyl effect.

\begin{center}
\includegraphics[width=0.7\textwidth]{scheme.png}
\end{center}

Scheme VI.6

In contrast to the direct addition of molecular bromine to cyclic vinylsilanes the mechanism with CuBr₂/CH₃CN appears more complex. We propose a mechanism as indicated in **Scheme VI. 7**
Cupric bromide in acetonitrile is known to form a green-colored trigonal bipyrimidal complex \([\text{CuBr}_3(\text{MeCN})_2]^+\).\(^{275}\) In our reactions, we continuously observe the presence of the green coloration indicating the formation of \([\text{CuBr}_3(\text{MeCN})_2]^+\). Therefore, in our CuBr\_2/CH\_3CN reactions, we propose that the cyclic vinylsilanes \(67-69\) first coordinate with copper bromide to form \(\pi\)-complex \([\text{a}]\).\(^{276}\) The green-colored trigonal bipyrimidal complex itself acts as bromide source for trans-attack at the \(\beta\)-position to the carbon bearing silicon \([\text{b}]\) as shown in \textit{path-1}. The \textit{trans}-attack leads to the formation of the anionic complex \([\text{c}]\) with the bromide substituted at the \(\beta\)-position to the silicon. Reductive conversion of cupric bromide to cuprous bromide leads to the formation of the neutral square planar complex \([\text{d}]\). Elimination of the mixed salt bromocuprousacetonitrile finally yields the \textit{trans}-1,2-dibromo-1-trimethylsilylcycloalkanes \(72 - 74\).

The formation of products \(72 - 74\) is once again reasoned to occur due to the conformational restrictions and geometrical constraints inherent in \(67 - 69\). Probably, the bromine and the trimethylsilyl- group cannot attain \textit{anti}-periplanar geometry for the smooth elimination of TMS-Br in the five- to seven- membered ring systems \(67 - 69\).

Thus, in the five- to seven-membered ring systems, the reactions give exclusively the 1,2-dibromo- adducts \(72-74\) while retaining the trimethylsilyl- group.

In the case of eight- and twelve- membered rings \(70\) and \(71\), due to large ring size and flexibility, the initial \(\pi\)-complex is attacked by the \([\text{CuBr}_3(\text{MeCN})_2]^+\) directly onto the trimethylsilyl-group \([\text{b}]\) as shown in \textit{path-2} directly leading to elimination of bromotrimethylsilane and formation of an anionic cycloalkenyl copper complex \([\text{e}]\). Further reduction of CuBr\_2 and formation of CuBr leads to the formation of the neutral square planar
cycloalkenyl copper complex. Reductive elimination of bromocuprousacetonitrile forms
the bromocycloalkenes 75 and 76.

Conclusions

The bromination reactions of simple cyclic vinylsilanes using cupric (II) bromide in
acetonitrile is reported. The effect of ring size over addition and substitution products is
discussed. From the results, we generalize that the five- to seven- membered common ring
cyclic vinylsilanes yield 1,2-dibromo-1-trimethylsilylcycloalkanes through addition in
approximately 73-87 % yields. However, in the eight- and twelve-membered large size
rings, the formation of electrophilic substitution products: 1-bromocyclooctene and 1-
bromocyclododecene were observed, along with a minor amount of other isomeric
bromocompounds.
Experimental

**General procedure for bromination of cyclic vinylsilanes 67-71**

To a magnetically stirred ice-cold solution of 1 mmol of cyclic vinylsilanes **67-71** in a 100 mL two necked round bottomed flask fitted with a water cooled condenser protected by CaCl₂ guard tube was added CuBr₂ (2 mol equivalents) in acetonitrile (30 mL) over a period of 30 min. After completion of addition, the mixture was allowed to attain room temperature with continuous stirring over one hour. The reaction mixture was diluted with 100 mL of diethylether and stirred for another 30 min. The contents were transferred to water (150 mL) and extracted with ether (3 x 40 mL). The combined organic extracts were washed with NaHCO₃ (2 x 20 mL), brine (1 x 30 mL), dried (Na₂CO₃) and concentrated on a rotary evaporator. Bulb to bulb distillation under reduced pressure yielded **72-74**.

**1,2-Dibromo-1-trimethylsilylcyclopentane 72**

Yield 0.16 g. 76%; IR 2952, 2898, 1434, 1407, 1249 (ν c·s), 1193, 1143, 1097, 1037, 973, 929, 842, 756, 690, 628; ¹H NMR 4.85-4.84 (d, 1H, J = 5.2 ), 2.96-2.98 (m, 1H), 2.53-2.45 (m, 1H), 2.31-2.22 (m, 2H), 2.10-2.06 (m, 2H); ¹³C NMR 62.1, 37.0, 35.8, 21.8, -0.6 GC-MS: 221 (1), 219 (1), 162 (1), 160 (1), 148 (11), 146 (13), 139 (20), 137 (20), 125 (6), 109 (6), 97 (8), 73 (91), 67 (100), 45 (19), 43 (20), 41 (13); Anal. Calcd. for C₆H₁₆Br₂Si: C, 32.02; H, 5.37 Found C, 31.89; H, 5.17.
**IR spectrum of 1,2-dibromo-1-trimethylsilylcyclopentane 72**

![IR spectrum image]

**$^1$H NMR spectrum of 1,2-dibromo-1-trimethylsilylcyclopentane 72**

![NMR spectrum image]
$^{13}$C NMR spectrum of 1,2-dibromo-1-trimethylsilylcyclopentane 72

\[ \text{GC-MS spectrum of 1,2-dibromo-1-trimethylsilylcyclopentane 72} \]

1,2-Dibromo-1-trimethylsilylcyclohexane 73$^{268}$

Yield 0.18 g, 78%; IR 2937, 2864, 1431, 1249 (υ C=Si), 1193, 1176, 1020, 908, 891, 842, 756, 690, 646; $^1$H NMR 4.75 (s, 1H), 2.75-2.69 (m, 1H), 2.22-2.16 (m, 1H), 1.94-1.85 (m, 4H), 1.64-1.58 (m, 2H), 0.25 (s, 9H); $^{13}$C NMR 57.6, 31.0, 29.0, 20.9, 20.1, 11.4 GC-MS: 235 (3), 233 (3), 203 (1), 162 (5), 160 (6), 139 (12), 137 (10), 125 (2), 123 (2), 109 (4), 81 (100), 79

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(41), 73 (59), 59 (12), 53 (15), 41 (10). Anal. Caled. For CsH18Br2Si : C, 34.41; H, 5.7 8:
Found C, 34.29 ; H, 5.45.

IR spectrum of 1,2-dibromo-1-trimethylsilylcyclohexane 73²⁶⁸

¹H NMR spectrum of 1,2-dibromo-1-trimethylsilylcyclohexane 73²⁶⁸
$^{13}$C NMR spectrum of 1,2-dibromo-1-trimethylsilylcyclohexane 73

GC-MS spectrum of 1,2-dibromo-1-trimethylsilylcyclohexane 73
1,2-Dibromo-1-trimethylsilylcycloheptane 74

Yield 0.21 g, 85% IR 2931, 2862, 1454, 1247 (v c.s.), 1190, 1161, 1012, 943, 854, 754, 688, 626; 1H NMR 4.84-4.83 (d, 1H, J = 4.4), 2.71-2.68 (m, 1H), 2.14-2.04 (m, 3H), 1.96-1.91 (m, 2H), 1.79-1.65 (m, 4H); 13C NMR 71.6, 62.8, 34.1, 33.5, 26.0, 23.8, 23.2, -0.7 GC-MS: 249 (1), 247 (1), 176 (1), 174 (1), 153 (1), 138 (4), 136.90 (4), 125 (1), 123 (1), 109 (3), 95 (100), 73 (91), 67 (54), 55 (18), 41 (23) Anal. Cald. For C9H10Br2Si: C, 36.60; H, 6.14; Found C, 36.45; H, 5.94.

IR spectrum of 1,2-dibromo-1-trimethylsilylcycloheptane(74)
$^1$H NMR spectrum of 1,2-dibromo-1-trimethylsilylcycloheptane 74

$^{13}$C NMR spectrum of 1,2-dibromo-1-trimethylsilylcycloheptane 74

GC-MS spectrum of 1,2-dibromo-1-trimethylsilylcycloheptane 74