Synthesis and spectral characterization of some silicon(IV) aryloxides

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Silicon (IV) aryloxides of the types \( \text{Me}_n\text{Si(OC}_6\text{H}_3\text{Me}_2-3,5\text{n} \), \( \text{OC}_6\text{H}_2\text{Me}_3-2,4,6\text{n} \), \( \text{OC}_6\text{H}_3\text{But}_2-2,6\text{n} \) (where \( n = 1, 2 \) and \( 1 \)), \( \text{Si(OC}_6\text{H}_3\text{Pr}_2-2,6\) \), \( \text{Cl}_2\text{Si(OC}_6\text{H}_3\text{Bu}_2-2,6\) \) and \( \text{Cl}_3\text{Si(OC}_6\text{H}_3\text{Bu}_2-2,6\) \) have been prepared by chloride-aryloxide exchange reactions and characterized by elemental analysis, molecular weight measurements, IR and \( ^1\text{H}, ^{13}\text{C} \) and \( ^{29}\text{Si} \) NMR studies.

The studies on silicon aryloxides with varying steric demands are not yet available except the work of Healy and co-workers\(^1\) on Si(IV) aryloxides. We report herein for the first time the detailed investigations on the synthesis and characterization of aryloxo derivatives containing organosilicon (IV) and silicon (IV) moieties. These studies are of special interest because of the growing and interesting role of Si-O-C bonded species as precursors for ceramics and glasses\(^2\).

Experimental

Stringent precautions were taken to exclude moisture throughout the experimental procedure. Benzene and \( n \)-hexane were dried by refluxing over sodium/benzophenone, followed by distillation. The chlorosilanes \( \text{Me}_3\text{SiCl} \) (b.p. 60°C), \( \text{Me}_2\text{SiCl}_2 \) (b.p. 70°C), \( \text{MeSiCl}_3 \) (b.p. 67°C), \( \text{SiCl}_4 \) (b.p. 57°C) used in this study were from Fluka and distilled (at temperatures given in parentheses) under atmospheric pressure before use. Phenols were recrystallised (from \( n \)-hexane) or distilled under reduced pressure. Silicon was estimated as silicon oxide\(^3\). IR spectra (4000-200 cm\(^{-1}\)) were recorded as Nujol mulls on Perkin-Elmer 557 spectrophotometers. \( ^1\)H(89.55 MHz), \( ^{13}\text{C} \) (22.49 MHz) and \( ^{29}\text{Si} \) (17.75 MHz) NMR spectra were recorded on a JEOL FX 90Q NMR spectrometer in CDC\(_3\) using TMS as an internal reference.

Synthesis of organosilicon aryloxides

Due to the similarity in the preparative procedure for a number of derivatives, only typical preparations are being detailed below for the sake of brevity. Further details have been listed in Table 1.

\[ \text{Me}_3\text{Si(OC}_6\text{H}_3\text{Me}_2-3,5\) ]

3,5-Dimethylphenol (2.82g, 25.03 mmol) and pyridine (1.98g, 23.1 mmol) in benzene (\( \sim 20\)ml) was added to a solution of \( \text{Me}_3\text{SiCl} \) (1.52g, 11.87 mmol) in benzene (\( \sim 30\) ml) and the reaction mixture was allowed to stir at room temperature for 12h, followed by refluxing for 1h. The precipitated \( \text{C}_6\text{H}_5\text{N.HCl} \) (2.38g, 20.69 mmol) was removed by filtration. After removal of the volatiles under reduced pressure, \( \text{Me}_3\text{Si(OC}_6\text{H}_3\text{Me}_2-3,5\) ] was obtained as a colourless liquid (3.42g, 96%), which distilled at 120°C/0.8 mm in 95% yield.

Adopting the above procedure derivatives \( \text{Me}_2\text{Si(OC}_6\text{H}_3\text{Pr}_2-2,6\) ] \( \) (b.p. \( \sim 110\)°/0.05 mm), \( \text{Me}_2\text{Si(OC}_6\text{H}_2\text{Me}_3-2,4,6\) ] (b.p. \( \sim 120\)°/0.8 mm), \( \text{Me}_2\text{Si(OC}_6\text{H}_3\text{Pr}_2-2,6\) ] (b.p. \( \sim 85\)°/0.9 mm), \( \text{Me}_3\text{Si(OC}_6\text{H}_3\text{Pr}_2-2,6\) ] (m.p. \( \sim 95\)°), \( \text{Cl}_2\text{Si(OC}_6\text{H}_3\text{Bu}_2-2,6\) ] (m.p. \( \sim 90\)°), \( \text{Cl}_3\text{Si(OC}_6\text{H}_3\text{Bu}_2-2,6\) ] (m.p. \( \sim 85\)°) were also prepared.

The preparative and analytical details are listed in Table 1. 

\[ \text{Si(OC}_6\text{H}_3\text{Pr}_2-2,6\) ]

To a benzene (\( \sim 20\)ml) solution of \( \text{SiCl}_4 \) (1.34g, 7.9 mmol), was added KO\(_2\text{H}_3\text{Pr}_2-2,6\) ] (prepared by refluxing K[1.23g, 31.41 mmol] and phenol [5.60g, 31.42 mmol] in tetrahydrofuran). After refluxing the reaction mixture for 20h, the precipitated \( \text{KCl} \) (2.31g, 22.40 mmol) was removed by filtration. The excess solvent was stripped off to yield light yellow crystalline \( \text{Si(OC}_6\text{H}_3\text{Pr}_2-2,6\) ] (5.57g, 96%) which was rec-
Table I—Characterization data* of aryloxo derivatives of silicon (IV)

<table>
<thead>
<tr>
<th>Sl. no.</th>
<th>Reactants</th>
<th>Product</th>
<th>Yield (%)</th>
<th>B.P./°C/mm Hg</th>
<th>Found (Calc), %</th>
<th>Mol. wt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g, mmol)</td>
<td>(Colour &amp; state)</td>
<td></td>
<td></td>
<td>Si  C  H</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Me₅SiCl₄ + 2HOCl₆Me₂-3,4</td>
<td>+ 2CH₃NH₂</td>
<td>Me₅Si(OCH₃Me₂-3,4)₂</td>
<td>4.05 (90)</td>
<td>120°/0.8</td>
<td>9.39</td>
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<tr>
<td>(192,14,99)</td>
<td>(3.41,27,99)</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>Me₂SiCl₃ + 2HOCl₆Me₂-3,5</td>
<td>+ 2CH₃NH₂</td>
<td>Me₂Si(OCH₃Me₂-3,5)₂</td>
<td>3.39 (95)</td>
<td>120°/0.8</td>
<td>9.30</td>
</tr>
<tr>
<td>(122,18,7)</td>
<td>(2.82,25,03)</td>
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<td></td>
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</tr>
<tr>
<td>3</td>
<td>Me₅SiCl₄ + 2HOCl₆Pr₂-2,6</td>
<td>+ 2CH₃NH₂</td>
<td>Me₅Si(OCH₃Pr₂-2,6)₂</td>
<td>2.33 (73)</td>
<td>110°/0.6</td>
<td>6.80</td>
</tr>
<tr>
<td>(126,19,8)</td>
<td>(3.46,19,39)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>4</td>
<td>Me₂SiCl₃ + 2HOCl₆Pr₂-2,6-4,6</td>
<td>+ 2CH₃NH₂</td>
<td>Me₂Si(OCH₃Pr₂-2,6-4,6)₂</td>
<td>3.32 (83)</td>
<td>135°/0.8</td>
<td>8.59</td>
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<tr>
<td>(154,1,03)</td>
<td>(3.28,24,10)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>5</td>
<td>MeCl₃ + HOCl₆Pr₂-2,6</td>
<td>+ CH₃N</td>
<td>MeCl₃(OCH₃Pr₂-2,6)₂</td>
<td>3.58 (85)</td>
<td>85°/0.9</td>
<td>11.20</td>
</tr>
<tr>
<td>(14,4,6)</td>
<td>(3.01,6,88)</td>
<td></td>
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</tr>
<tr>
<td>6</td>
<td>Me₃Cl + HOCl₆Pr₂-2,6</td>
<td>+ CH₃N</td>
<td>Me₃Cl(OCH₃Pr₂-2,6)₂</td>
<td>5.43 (97)</td>
<td>95°</td>
<td>4.85</td>
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<tr>
<td>(1,44,9,7)</td>
<td>(5.16,28,95)</td>
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<tr>
<td>7</td>
<td>SiCl₄ + 3HOCl₆Pr₂-2,6</td>
<td>+ 3CH₃N</td>
<td>C₃Si(OCH₃Pr₂-2,6)₃</td>
<td>4.87 (98)</td>
<td>85°</td>
<td>4.70</td>
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<tr>
<td>(132,8,36)</td>
<td>(4.44,24,9)</td>
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<tr>
<td>8</td>
<td>SiCl₄ + 4HOCl₆Pr₂-2,6</td>
<td>+ 4CH₃N</td>
<td>Si(OCH₃Pr₂-2,6)₄</td>
<td>5.57 (96)</td>
<td>90°</td>
<td>3.80</td>
</tr>
<tr>
<td>(134,7,9)</td>
<td>(5.60,31,42)</td>
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<tr>
<td>9</td>
<td>SiCl₄ + HOCl₆Bu₂-2,6</td>
<td>+ CH₃N</td>
<td>Cl₃Si(OCH₃Bu₂-2,6)₂</td>
<td>1.09 (85)</td>
<td>85°</td>
<td>8.25</td>
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<tr>
<td>(0.69,4)</td>
<td>(0.78,3,7)</td>
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<tr>
<td>10</td>
<td>Me₅SiCl₄ + 2HOCl₆Bu₂-2,6</td>
<td>+ 2K</td>
<td>Me₅Si(OCH₃Bu₂-2,6)₂</td>
<td>3.00 (57)</td>
<td>132°/0.7</td>
<td>5.94</td>
</tr>
<tr>
<td>(14,1,78)</td>
<td>(6.43,22,48)</td>
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<tr>
<td>11</td>
<td>Me₅SiCl₄ + 2HOCl₆Bu₂-2,6-4,6</td>
<td>+ 2K</td>
<td>Me₅Si(OCH₃Bu₂-2,6-4,6)₂</td>
<td>1.31 (52)</td>
<td>140°/0.7</td>
<td>4.85</td>
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<tr>
<td>(1,75,3,9)</td>
<td>(2.65,9,98)</td>
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<tr>
<td>12</td>
<td>SiCl₄ + 2HOCl₆Bu₂-2,6</td>
<td>+ 2K</td>
<td>C₃Si(OCH₃Bu₂-2,6)₃</td>
<td>3.50 (85)</td>
<td>92°</td>
<td>5.46</td>
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<tr>
<td>(1,37,8,6)</td>
<td>(1.32,16,9)</td>
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</table>

* Calculated values in parenthesis.  

Results and discussion

The reactions in desired molar ratios of chloro- 
lanes with appropriate substituted phenyl in the pres- 
ence of pyridine in benzene afford aryloxo deriva- 
tives according to the following general reaction:

\[ \text{R}_n \text{SiCl}_4 + n \text{ArOH} + n\text{CH}_3\text{N} \rightarrow \text{R}_n\text{Si(OAr)}_n + n\text{CH}_3\text{NHCl} \]

(1) R = Me, n = 2, OAr = OCH₃Me₂-3,4
(2) R = Me, n = 2, OAr = OCH₃Me₂-3,5
(3) R = Me, n = 2, OAr = OCH₃Pr₂-2,6
(4) R = Me, n = 2, OAr = OCH₃Me₂-2,6-4,6
(5) R = Me, n = 1, OAr = OCH₃Pr₂-2,6
(6) R = Me, n = 3, OAr = OCH₃Pr₂-2,6
(7) R = Cl, n = 3, OAr = OCH₃Pr₂-2,6
(8) R = Cl, n = 4, OAr = OCH₃Pr₂-2,6
(9) R = Cl, n = 1, OAr = OCH₃Bu₂-2,6

In view of the failure of 1/2 reaction between 
Me₅SiCl₄ (or SiCl₄) and HOCl₆Bu₂-2,6 in the pres- 
ence of pyidine, the desired derivatives were pre- 
pared according to the reactions described below:

\[ \text{MeCl₃ + 2KOC}_6\text{H}_4\text{Bu₂-2,6} \rightarrow \text{Me₅Si(OAr)}_2 + 2\text{KCl} \]
(10) OAr = OC₆H₄Bu₂-2,6
(11) OAr = OC₆H₄Bu₂-2,4,6

\[ \text{SiCl₄ + 2KOC}_6\text{H}_4\text{Pr₂-2,6} \rightarrow \text{SiCl₅(OAr)}_2 + 2\text{KCl} \]
(12) OAr = OC₆H₄Pr₂-2,6

Although derivatives SiCl₅(OAr)₂ and 
Si(OAr)₂Pr₂-2,6 could be prepared using pyridine as 
a proton acceptor, it took ~26h and 48h, respect- 
ively for completion of the reaction.

An alternative convenient route for the synthesis of 
such derivatives has been the reaction of SiCl₄ and 
KOC₆H₄Pr₂-2,6 in desired molar ratios in benzene: 

\[ \text{SiCl₄ + nKOC}_6\text{H}_4\text{Pr₂-2,6} \rightarrow \text{SiCl₅(OAr)}_n + n\text{KCl} \]

n = 3,4

These derivatives are highly moisture sensitive, 
colourless liquids to yellowish white crystalline solids, 
soluble in common organic solvents (e.g., benzene, 
toluene, dichloromethane, n-hexane, etc.) and mon- 
omeric (ebullioscopically in benzene).
The $^1$H NMR spectra of the organosilicon aryloxides, show no resonance due to phenolic OH, in the region $\delta$ 4.47-5.29 indicating deprotonation of OH protons. The chemical shifts of aromatic ring protons in the region $\delta$ 6.44-7.51 are almost unaltered compared with those observed for the corresponding parent phenols ($\delta$ 6.53-7.51).

The silicon-methyl signals observed in the range $\delta$ 0.27-0.58 exhibit deshielding with increase in the number of aryloxo moieties attached to the silicon centre. Similar observations were earlier observed for tetrahedral derivatives such as Me$_4$SiCl$^-$ [ref. 4], and Me$_3$SiON ($\delta$ = CEt$_2$) [ref. 5]. The observed trend for the CH$_2$Si chemical shifts ($\delta$): Me$_2$SiOAr*$_n$ < Me$_2$Si(OAr)$_n$ < Me$_2$Si(OEt)$_n$ ($\delta$ where OAr* = OC$_6$H$_3$Pri$_2$-$t$) suggests the predominance of the $\pi$ and steric effects over the possibility of (p-d) hybridization from oxygen to silicon centre rather than the delocalization of oxygen lone pair to the $\pi$ orbital of the aromatic ring.

The above infrared [10-14] and nuclear magnetic resonance [6,8,9] assignments, which have been made on the basis of published data and molecular weight measurements indicate a tetrahedral $sp^3$ hybridization around the silicon in all these new aryloxide derivatives.

Acknowledgement

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References

(c) Brinker C J, Clark D E & Ulrich D R, Better ceramics through chemistry II (Materials Research Society, Pittsburgh, PA), 1986.