Electronic Supplementary Information

of the ‘full paper’ in the journal New Journal of Chemistry entitled:

Selective Ring Opening of 4H-1,3,2-Benzodioxasiline Twin Monomers

by the authors:

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Table of Content

1. Mass spectrograms of 1b, 2b, and 3b

2. Chirality and stereochemical aspects of 1a and 3a
   2.1. Chirality and diastereotopic hydrogens of 1a and 3a
   2.2. Geminal coupling of diastereotopic hydrogens of 1a and 3a in 1H NMR

3. Screening for appropriate electrophiles / Additional polymerization information

4. Additional NMR information
   4.1. Additional NMR information about 1b
   4.2. Additional NMR information about 2b
   4.3. Additional NMR information about 3b

5. Side products – NMR information

6. Derivatization of 2b
   6.1. with 1-methylimidazole
   6.2. with tetra-n-butylammonium acetate
   6.3. with bromine

7. Supplementary References
1. Mass spectrograms of 1b, 2b, and 3b

Supplementary Figure 1. Mass spectrograms of 1b, 2b, and 3b in their reaction mixtures. The spectrograms differ heavily, if the ionization method is slightly reinforced as shown for 1b.

2. Chirality and stereochemical aspects of 1a and 3a

2.1. Chirality and diastereotopic hydrogens of 1a and 3a

Supplementary Figure 2. Spiro monomers 1a and 3a are racemic mixtures of the depicted enantiomers. The two hydrogens of the methylene group are not equivalent, one facing to the methylene group of the neighbor ring, the other one to the opposite direction.

2.2. Geminal coupling of diastereotopic hydrogens of 1a and 3a in $^1$H NMR

Supplementary Figure 3. $^1$H NMR (400 MHz) of 1a in CDCl$_3$.

Because of the non-equivalence of the hydrogens at the methylene group of 1a and 3a, their chemical shifts differ slightly in the $^1$H NMR spectroscopy. Due to geminal coupling ($^2$J), each hydrogen shows a doublet signal. Because of the relative small difference in chemical shift a strong roofing effect occurs. At $B_0 = 250$ MHz 1a seemed to show only one broad singlet for the methylene group, but at $B_0 = 400$ MHz it becomes obvious that actually two very close
doublets are present. For 3a measurement at $B_0$ = 250 MHz was sufficient enough, because the chemical shifts of the hydrogens differ more compared to 1a. Therefore the roofing effect is observable, but less pronounced as in the case of 1a, the signals resemble a quartet signal.

![3a_1H NMR_250 MHz](image)

Supplementary Figure 4. $^1$H NMR (250 MHz) of 3a in CD$_2$Cl$_2$.

Calculations relate on equations (1) and (2).\(^{[12]}\)

$$\nu_1 - \nu_3 = \nu_2 - \nu_4 = \sqrt{(\nu_a - \nu_b)^2 + J^2}$$

(1)

$$\nu_m = \frac{1}{2}(\nu_a + \nu_b) = \frac{1}{2}(\nu_1 + \nu_4) = \frac{1}{2}(\nu_2 + \nu_3)$$

(2)

### 3. Screening for appropriate electrophiles

As mentioned in the article several electrophiles were tested for their ability to react with 4H-benzo-1,3,2-dioxasilines and to form stable ring-opened species. Because of practical aspects the screening was tested with compound 2a, which is liquid at room temperature and easier to synthesize and to purify than 1a and 3a. In order to avoid Brønsted acids we preferred to test iodomethane (CH$_3$I), dimethylsulfate (DMS) and chlorotrimethylsilane ((CH$_3$)$_3$Si-Cl). Finally, the use of the more reactive iodotrimethylsilane ((CH$_3$)$_3$Si-I) led to ring-opened benzyl iodide species, which were stable enough to get fully analyzed before they were consumed by a slow polymerization process forming phenolic resin.

**Supplementary Table 1.** Screening experiments for the ability of different electrophiles to ring-open 4H-1,3,2-benzodioxasiline (tested with 2,2-dimethyl-4H-1,3,2-benzodioxasiline (2a))

<table>
<thead>
<tr>
<th>m (n) (2a)</th>
<th>m (n) (electrophile)</th>
<th>solvent</th>
<th>$^9$</th>
<th>result ($^1$H,$^{13}$C NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.79 g (0.060 mol)</td>
<td>8.50 g (0.060 mol) CH$_3$I + 1 g (0.008 mol) DMS</td>
<td>20 ml CH$_2$Cl$_2$</td>
<td>25°C</td>
<td>+ 4 h: unreacted educts</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+ 15 h: unreacted educts</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+ 5 d: unreacted educts</td>
</tr>
<tr>
<td>7.23 g (0.040 mol)</td>
<td>5.06 g (0.040 mol) DMS</td>
<td>-</td>
<td>85°C</td>
<td>+ 1 h: polymer (pink solid)</td>
</tr>
<tr>
<td>3.57 g (0.020 mol)</td>
<td>2.81 g (0.020 mol) CH$_3$I</td>
<td>10 ml toluene</td>
<td>85°C</td>
<td>+ 2 h: unreacted educts</td>
</tr>
<tr>
<td>0.65 g (0.004 mol)</td>
<td>0.39 g (0.004 mol) (CH$_3$)$_3$Si-Cl</td>
<td>-</td>
<td>25°C</td>
<td>+ 1 h: unreacted educts</td>
</tr>
<tr>
<td>0.56 g (0.003 mol)</td>
<td>0.62 g (0.003 mol) (CH$_3$)$_3$Si-I</td>
<td>-</td>
<td>25°C</td>
<td>after ~40 min: first measured $^1$H NMR spectrum confirmed almost complete conversion to ring-opened benzyl iodide; slowly polymerization to phenolic resin</td>
</tr>
</tbody>
</table>

$M(2a) = 180.28$ g/mol
After addition of iodotrimethylsilane to stirred 2a, the reaction mixture turned immediately brownish indicating a beginning reaction, and probably the formation of spurious iodine causes the brownish color. After 40 min the reaction mixture was analyzed by $^1$H, $^{13}$C, and $^{29}$Si NMR, the results confirmed a nearly quantitative conversion of 2a and iodotrimethylsilane to a ring-opened benzyl iodide. A slow polymerization process takes place while the reaction mixture was kept at 25°C. Precipitates of solid moieties of phenolic resin were forming the next hours and days. The soluble part (in CDCl$_3$) of the kept NMR tube shows a small ratio of not consumed benzyl iodide 2b and phenolic resin (see Supplementary Figure 5). It is assumed that hydroiodic acid, which is liberated during the polymerization of benzyl iodide to phenolic resin, is reacting with left silyl ether groups. Probably iodosilanes form again, comparable to a catalytic regeneration, and show a chemical $^1$H NMR shift of $\delta \sim 0.9$ ppm.

Supplementary Figure 5. $^1$H NMR analysis ($\delta$(CDCl$_3$) = 7.26 ppm) of the first successful ring-opening reaction of 2a using iodotrimethylsilane as electrophile as mentioned in Supplementary Table 1. Short time stable benzyl iodide 2b was identified.

4. Additional NMR information

4.1. Additional NMR information about 1b

Supplementary Figure 6. Magnified sections of the $^{13}$C NMR spectrum of 1b (the complete spectrum is depicted in Figure 1 in the article; reference CD$_2$Cl$_2$ $\delta = 54.0$ ppm). At this magnification three very close lying signals at $\delta \sim 130.5$ ppm become distinguishable. The signal of the trimethylsilyl group of 1b is found at $\delta = 2.14$ ppm, close to the signal of the iodomethylene group at $\delta = 1.72$ ppm. Signal assignments were assured by additional $^1$H/$^{13}$C-HMQC NMR. Side products containing trimethylsilyl groups show also signals in this region (see chapter 5.).
Supplementary Figure 7. $^1$H/$^{13}$C-HMQC NMR spectrum of 1b (in CD$_2$Cl$_2$) and magnified sections.

4.2. Additional NMR information about 2b

Supplementary Figure 8. Magnified sections of the $^{13}$C NMR spectrum of 2b (the complete spectrum is depicted in Figure 1 in the article; reference CD$_2$Cl$_2$ $\delta = 54.0$ ppm). At this magnification three very close lying signals at $\delta \sim 130.5$ ppm become distinguishable. The signal of the trimethylsilyl group of 2b is found at $\delta = 2.13$ ppm, close to the signal of the dimethylsilyl group at $\delta = 0.25$ ppm, and close to the signal of the iodomethylene group at $\delta = 2.38$ ppm. Signal assignments were assured by additional $^1$H/$^{13}$C-HMQC NMR.

Supplementary Figure 9. $^1$H/$^{13}$C-HMQC NMR spectrum of 2b (in CD$_2$Cl$_2$) and magnified sections.
4.3. Additional NMR information about 3b

Supplementary Figure 10. Magnified sections of the $^{13}$C NMR spectrum of 3b (the complete spectrum is depicted in Figure 1 in the article; reference CD$_2$Cl$_2$ $\delta = 54.0$ ppm). At this magnification three very close lying signals at $\delta \sim 131.5$ ppm become distinguishable. The signal of the trimethylsilyl group of 3b is found at $\delta = 1.84$ ppm, close to the signal of the iodomethylene group at $\delta = 4.84$. Signal assignments were assured by additional $^1$H/$^{13}$C-HMQC NMR. Side products containing trimethylsilyl groups show also signals in this region (see chapter 5.).

Supplementary Figure 11. $^1$H/$^{13}$C-HMQC NMR spectrum of 3b (in CD$_2$Cl$_2$) and magnified sections.

5. Side products - NMR information

As discussed in the article, the higher dilution of 3b in CD$_2$Cl$_2$ and its sterical properties lead to a slower ring opening reaction and therefore more side reactions of iodotrimethylsilane can occur. Reactions with the glass of the flasks will lead to trimethylsilanol (TMS-OH), hexamethyldisiloxane (TMS$_2$O), and tetrakis(trimethylsiloxy)silane (TMSO$_4$Si). Exemplarily, the additional signals in the $^{29}$Si NMR of 3b (see Figure 1) confirm this assumption: $\delta$ [ppm] = 14.2 (TMS-OH), 7.5 (TMS$_2$O), $-104.6$ (TMSO$_4$Si). Probably due to an only single ring opened species of 3a the signal at $\delta = -93.5$ ppm is found.

Supplementary Table 2. NMR overview of possible trimethylsilyl side products (TMS species, as mentioned in the article) and their chemical shifts ($\delta$ in ppm).

<table>
<thead>
<tr>
<th></th>
<th>$^1$H NMR</th>
<th>$^{13}$C NMR</th>
<th>$^{29}$Si NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference</td>
<td>[14]</td>
<td>[14]</td>
<td></td>
</tr>
<tr>
<td>TMS-OH</td>
<td>0.11</td>
<td>0.12, 4.11</td>
<td>-</td>
</tr>
<tr>
<td>TMS$_2$O</td>
<td>0.04</td>
<td>0.09</td>
<td>6.53</td>
</tr>
<tr>
<td>TMSO$_4$Si</td>
<td>0.11</td>
<td>-</td>
<td>8.62, $-104.08$</td>
</tr>
<tr>
<td>TMS-I</td>
<td>0.78</td>
<td>0.80</td>
<td>8.7</td>
</tr>
</tbody>
</table>
6. Derivatization of 2b

As mentioned in the article the ring-opened compounds 1b, 2b, and 3b tend to polymerize because of the unstable iodomethylene groups. Additionally to their reactivity the formation of hydroiodic acid leads to further side reactions as the attack and cleavage of the siloxy groups. Especially, more polar solvents and high concentrations have to be avoided. To prove additionally the presence of the reactive benzyl iodides, they can be transformed to more stable compounds.

The use of several silver salts for ion exchange experiments failed, more polar solvents were used and polymerization proceeded rapidly.

Appropriate reagents represent neutral nucleophiles. 1-Methylimidazole was used, it attacks the electrophile iodomethylene group forming an imidazolium salt with iodide as anion. This way the polymerization tendency is vanished and the only molecular instability of the imidazolium cation is due to the possible hydrolysis of the siloxy-groups.

→ see chapter 6.1.

Another possibility is the use of a nucleophilic anion, but due to the instability of 2b in polar solvents the anion must be diluted in a non-polar solvent. This discrepancy can be overcome when the properties of the cation enable phase transfer. Therefore tetra-n-butylammonium acetate was applied and the reaction with 2b to the stable benzyl acetate succeeded.

→ see chapter 6.2.

Another attempt to derivatize the benzyl iodide 2b was the use of bromine in order to create less reactive benzyl bromides. The use of chlorine and fluorine was excluded for practical work. After some attempts that failed a good method was found for the synthesis of the corresponding benzyl bromide, but the product is still very unstable and polymerizes, too. The mechanism is not fully clear yet. Like in ionic iodine compounds the iodide ion can be oxidized by stronger oxidative compounds like bromine, chlorine, and fluorine. One can assume that the strong polarized iodomethylene group of 2b could be accessible to this reaction. Or spurious bromide ions attack as nucleophiles the iodomethylene group and liberate iodide ions, which again react with bromine to iodine and bromide ions.

→ see chapter 6.3.

6.1. Derivatization of 2b with 1-methylimidazole

Synthesis of 1-(2-((1,1,3,3,3-pentamethyldisiloxanyloxy)benzyl)-3-methylimidazolium iodide (2b/mim):

In a 50 ml flask at 25°C 0.947 g (5.2 mmol) 2a were stirred and 1.020 g (5.10 mmol) of iodotrimethylsilane were added with a syringe at once. After 5 min 10 ml of CH$_2$Cl$_2$ were added and a small sample (2 drops) of the diluted mixture was analyzed via $^1$H NMR spectroscopy. As expected the NMR data proved nearly quantitative consumption of 2a to 2b. Then, 0.412 g (5.02 mmol) of 1-methylimidazolide was added to the solution and the reaction mixture was continued to stir at $\vartheta = 25$ °C for 3 h. The solvent was removed under vacuum, and the residue was washed 5 times with 3 ml hexane. The obtained product is yellow oil. Yield: ~100% relative to the used 1-methylimidazole.

$^1$H NMR $\delta$(CD$_2$Cl$_2$) = 5.32 ppm]: 9.87 (1H, s(br),2-mim), 7.65-6.95 (6H, m), 5.46 (2H, s, CH$_2$), 4.02 (3H, s, mimCH$_3$), 0.26 (6H, s, Si(CH$_3$)$_2$), 0.07 (9H, s, Si(CH$_3$)$_3$):

$^{13}$C NMR $\delta$(CD$_2$Cl$_2$) = 54.0 ppm]: 153.7(C-O), 136.9 (N-CH-N), 131.8, 131.4, 123.9, 123.8, 122.5, 122.4, 119.5, 49.2 (CH$_2$), 37.3 (CH$_3$), 1.7 (Si(CH$_3$)$_2$), 0.0 (Si(CH$_3$)$_3$):

$^{29}$Si NMR $\delta$(TTSS, $^{29}$Si(CH$_3$)$_3$) = $-$9.8 ppm]: +10.6 (M$_1$), $-$11.0 (D$_1$);

m/z: 335.2 [M$^+$].

1-Methylimidazolide (99%) was used as purchased from Carl Roth GmbH & Co. KG.
**Supplementary Figure 13.** NMR data of 2b/mim measured in CD$_2$Cl$_2$. Spectra are referenced to CD$_2$Cl$_2$ $\delta$(H/13C) = 5.32/54.0 ppm and to TTSS $\delta$(29Si(CH$_3$)$_3$) = −9.8 ppm.

**Supplementary Figure 14.** Mass spectrogram (electrospray ionization) of 2b/mim.
6.2. Derivatization of 2b with tetra-\(n\)-butylammonium acetate

![Diagram]

**Supplementary Figure 15.** The nucleophilic attack of the acetate ion onto the iodomethylene group of 2b leads to the formation of 2c.

**Synthesis of 2-(acetoxy methyl) phenoxo trimethylsiloxy dimethylsilane (2c):**

Alternative name: 2-((1,1,3,3,3-pentamethyldisiloxanyl)oxy)benzyl acetate

Ring-opening reaction (as described in the article) followed by reaction with \(^{7}\text{Bu}_4\text{OAc}\):

In a 50 ml flask at 25°C 1.1712 g (6.50 mmol) of 2a are stirred and 1.2944 g (6.47 mmol) of iodomethyltrimethylsilane were added with a syringe at once. After 5 min 20 ml of chloroform were added and a small sample (2 drops) of the diluted mixture was analyzed in CD\(_2\)Cl\(_2\) via \(^1\text{H}\) NMR spectroscopy. As expected the NMR data proved nearly quantitative consumption of 2a to 2b. A solution of a small excess of tetra-\(n\)-butylammonium acetate (2.35g, 7.80 mmol) in 10 ml chloroform was then added to the reaction mixture at once (~9 min after addition of iodomethyltrimethylsilane, ~4 min after diluting the reaction mixture). The reaction mixture decolorized immediately and a second sample was analyzed by \(^1\text{H}\) NMR spectroscopy. It proved complete consumption of 2b. After 1 h the reaction mixture was filled into a 500ml flask with 150 ml hexane, and another 50 ml of hexane was used to wash the 50 ml flask and then was added to the 500 ml flask. The hexane solution was decanted and filtered off from the formed precipitates and all solvents were removed by evaporation under reduced pressure.

**Purifying the product:**

The first attempt to purify the product via distillation at 4 mbar failed, because as the necessary temperature of ~190°C was reached firstly clear colorless oil was obtained, but after some minutes the oil in the heated flask started to polymerize and a solid substance was formed. Acetic acid as condensation by-product had formed and was found in the cooling trap. The attempt was aborted and the recovered crude oil from the heated flask and the purified oil were mixed together and the distillation procedure was repeated at 0.1 mbar. Clear colorless oil was obtained at 0.1mbar / 120°C. The yield in this case was lowered by the first attempt of distillation and amounts only 33 % of theory.

As this was the first attempt to derivatize 2b with \(^{7}\text{Bu}_4\text{OAc}\) it is assumed that the yield can be increased to >80% in theory. The synthetic procedure and the purifying process can be improved.

**NMR data:**

\(^1\text{H}\) NMR \(\delta\) (CD\(_2\)Cl\(_2\)) = 5.32 ppm: 7.36-7.19 (2H, m, Aryl), 7.03-6.92 (2H, m, Aryl), 5.12 (2H, s, CH\(_2\)), 2.08 (3H, s, CH\(_3\)), 0.25 (6H, s, Si(CH\(_3\))\(_2\)), 0.13 (9H, s, Si(CH\(_3\))\(_3\));

\(^{13}\text{C}\) NMR \(\delta\) (CD\(_2\)Cl\(_2\)) = 54.0 ppm: 171.2 (C=O), 153.7 (C\(_{aryl}-\text{O}\)), 130.5, 129.9, 127.4, 122.0, 119.8, 62.5 (CH\(_2\)), 21.4 (CH\(_3\)), 1.9 (Si(CH\(_3\))\(_2\)), -0.1 (Si(CH\(_3\))\(_3\));

\(^{29}\text{Si}\) NMR \(\delta\) (TST, \(^{26}\text{Si}\)) = -9.8 ppm: +9.7 (M\(_3\)), -12.5 (D\(_1\)).

Tetra-\(n\)-butylammonium acetate (>99%) was used as purchased from Sigma-Aldrich.
Supplementary Figure 16. NMR data of 2c measured in CD$_2$Cl$_2$. Spectra are referenced to CD$_2$Cl$_2$ $\delta$(H/$^{13}$C) = 5.32/54.0 ppm and to TTSS $\delta$(Si(CH$_3$)$_3$) = −9.8 ppm.
6.3. Derivatization of 2b with bromine

**Supplementary Figure 17.** The reaction of 2b with bromine leads to the formation of the corresponding benzyl bromide 2d.

**Synthesis of 2-(bromomethyl)phenoxy-trimethylsiloxy-dimethylsilane (2d):**

Alternative name: 2-((1,1,3,3,3-pentamethyldisiloxanyl)oxy)benzyl bromide

Ring-opening reaction (as described in the article) followed by reaction with bromine:

In a 50 ml flask at 25°C 1.4857 g (8.24 mmol) of 2a were stirred and 1.590 g (7.95 mmol) of iodotrimethylsilane were added with a syringe at once. After 5 min 30 ml of hexane were added and a small sample (2 drops) of the diluted mixture was analyzed in CD$_2$Cl$_2$ via $^1$H NMR spectroscopy. As expected the NMR data proved nearly quantitative consumption of 2a to 2b. Then (~ 37 min after addition of iodotrimethylsilane, ~ 32 min after addition of hexane), 0.652 g (4.08 mmol) of bromine diluted in 0.5 ml of hexane was added by syringe at once to the reaction mixture. The former red transparent solution turned violet (I$_2$). A second sample was analyzed in CD$_2$Cl$_2$ by $^1$H NMR spectroscopy that proved consumption of the benzyl iodide to the benzyl bromide.

Unfortunately the reaction mixture was not stable and during the next hours the benzyl bromide polymerizes. But, the sample taken shortly after the addition of bromine, which was additionally diluted in CD$_2$Cl$_2$, stood unchanged. A $^1$H NMR spectrum after 15 h showed no difference. Improvements on the synthesis can be done, an even higher dilution grade is necessary to suppress the polymerization tendency.

It seems, that direct bromination of benzyl iodides is possible, although no literature could be found describing such a reaction with Br$_2$, only a similar reaction using BiBr$_3$ is known,[16] additionally a nucleophilic attack of spurious bromide cannot be excluded. The latter one would lead to a catalytic regeneration of bromide, because once iodide is liberated, it will react with bromine to iodine and bromide ions.

It is still unclear if this reaction is only applicable for our 2-iodomethyl phenoxy compounds (2-oxybenzyl iodides), which stabilize the polarized methylene carbon or for the whole substance class of benzyl iodides.

**NMR data (2d in hexane-solution):**

$^1$H NMR $\delta$(CD$_2$Cl$_2$) = 5.32 ppm: 7.38-7.14 (2H, m, Aryl), 7.00-6.90 (2H, m, Aryl), 4.55 (2H, s, CH$_2$Br), 0.30 (6H, s, Si(CH$_3$)$_2$), 0.15 (9H, s, Si(CH$_3$)$_3$);

$^{13}$C NMR $\delta$(CD$_2$Cl$_2$) = 54.0 ppm: 154.0 (C$_{Aryl}$=O), 131.6, 130.6, 129.2, 122.3, 120.1, 30.0 (CH$_2$Br), 2.0 (Si(CH$_3$)$_3$), 0.1 (Si(CH$_3$)$_2$).

Bromine (>99%) was used as purchased from Merck-Schuchardt OHG.
Supplementary Figure 18. NMR data of 2d measured in CD$_2$Cl$_2$. Spectra are referenced to CD$_2$Cl$_2$ $\delta^{(1\text{H/13C})} = 5.32/54.0$ ppm.

7. Supplementary References

14 NMR prediction program.
15 Own NMR results. Substances were measured in CD$_2$Cl$_2$ and spectra were referenced to CD$_2$Cl$_2$ $\delta^{(1\text{H/13C})} = 5.32/54.00$ ppm, and TTSS $\delta^{(29\text{SiMe}_3)} = -9.8$ ppm.