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A new synthesis of 1,3-dihydrobenzo[1,2]oxasiloles by a novel rearrangement of a pentavalent silicon intermediate

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A new synthesis of benzo[1,2]oxasiloles is described, wherein an unprecedented intramolecular allylic transposition takes place probably involving a pentavalent silicon intermediate.

Benzoxasiloles are interesting in their structure in that they contain the chemically labile O–Si and C–Si bonds, allowing for much derivatizing. Few methods for the synthesis of substituted benzoxasiloles have been reported, and in each case the preparations concerned mostly specific examples.[1–8]

We report herein a new, general synthesis of benzo[1,2]oxasiloles **1** (Fig. 1) from easily accessible *ortho*-silylated benzaldehydes **7a–c**, for which we also describe new preparations.

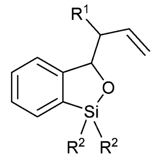

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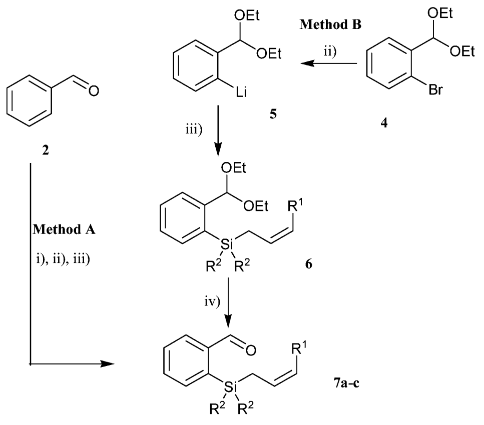
Fig. 1 3-Allylbenzo[1,2]oxasiloles.

The reaction sequence we employed is quite general, allowing possible substitution on the allylic group and the silicon atom. Other benzaldehydes could also be employed to prepare new functionalized analogues. In Scheme 1 is described the preparation of *ortho*-allylsilylbenzaldehydes by two different approaches. In the first case benzaldehyde **2** is silylated with chlorosilanes **3a–c** following orthometallation using *N*,*N*,*N′*-trimethylethylenediamine and n-butyllithium[9] (method A). In the second case, *ortho*-bromobenzaldehyde diethylacetal **4** undergoes a halogen–metal exchange using n-butyllithium, followed by silylation to give acetals **6**. Acid hydrolysis then furnishes the required *ortho*-substituted benzaldehydes **7** (method B). In both cases, the overall yields are good (Table 1), while the latter, two-step approach is generally higher yielding overall. In addition, a *ortho-vinyl*silyl benzaldehyde **7d** was also prepared by the above procedures.



Scheme 1 Synthetic scheme for the preparation of 2-silyl benzaldehydes. i) $LiNMeCH_2CH_2NMe_2$, THF, −78 °C, ii) nBuLi then iii) chlorosilane **3a–3c**; iv) iPrOH, H_2O, THF, TsOH.

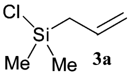
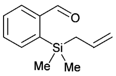
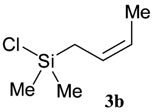
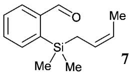
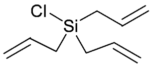
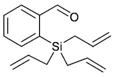
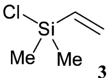
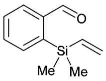
Silane derivatives **7a** and **7b** are then heated in toluene or xylene to effect the observed rearrangement into benzo[1,2]oxasiloles (Scheme 2). Interestingly, in one case, during the preparation of required arylallylsilane **7c** (entry 3), spontaneous rearrangement under the experimental conditions (THF, 20°C), provided **1c** directly (see later). As a test experiment for mechanistic elucidation, we also treated the *vinylic* analogue **7d** in the same manner. Indeed no reaction was observed and starting material was totally recovered, which concurs with the proposed mechanism.

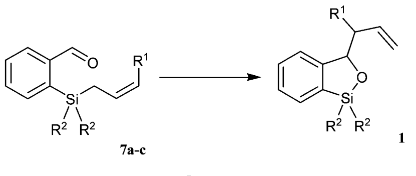
Following the thermal reaction, in the cases of **7a** and **7b** the required 3-allyl benzo[1,2]oxasiloles **1a** (R^1 = H; R^2 = Me) and **1b** (R^1 = R^2 = Me) were obtained in 96% and 70% yields, respectively (Table 2). In the latter example, the remainder of the yield corresponds to recovered starting benzaldehyde **7b**. **1c** was obtained in 38% overall yield, directly from benzaldehyde **2**, without isolation of the corresponding *ortho*-allylsilyl benzaldehyde **7c**.

We propose a mechanism (Scheme 3) for the observed transformation by which an intermediate pentavalent silicon is formed,[1,7] followed by a "nucleophilic" intramolecular allylic transposition.

From the observed results, it appears that the groups present on the silicon atom can influence the yield and the ease of reaction. **2b** containing a *Z* crotyl group gave a single product albeit in lower yields certainly due to the added steric bulk of the methyl substituent on the attacking allyl moiety. It is proposed that pentavalent silicon adopts a trigonal bipyramidal configuration[1,7] (Fig. 2) in which the oxygen atom occupies an axial position and that the allylic group must have an equatorial arrangement in order to transpose to the cationic benzylic methylene. A pseudo-equilibrium (rearrangement) would assure that such a relative

Table 1 *ortho*-Allyl- and vinylsilyl benzaldehydes **7a–d**

Entry	Chlorosilane[10,11]	Compound	Yield (method A) (%)	Yield (method B) (%)
1	 **3a**	 **7a**	51	87
2	 **3b**	 **7b**	71	n/a
3	 **3c**	 **7c**	other product (**1c**)	n/a
4	 **3d**	 **7d**	67	87



Scheme 2

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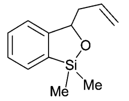
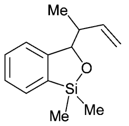
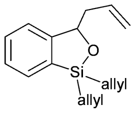
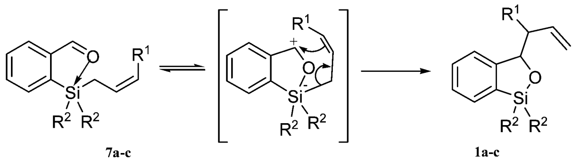
Table 2 Benzo[1,2]oxasiloles

Entry	Product	Solvent, Temp./°C	Time/h	Yield (%)
1	 **1a**	Toluene, 110	14	96
2	 **1b**	Xylene, 140	24	70
3	 **1c**	THF, 20[a]	4	38

[a] Obtained by spontaneous transposition during the previous step.



Scheme 3 Proposed pentavalent silicon mechanism.

configuration can occur. The ease of reaction observed for the triallyl analogue would suggest that such a sequence is plausible, since at all times one allyl group is at an equatorial position. Furthermore, formation of **1b** as the only product confirms the concerted intramolecular character of the allylic transposition.

No precedent for this type of allylic rearrangement has been described to our knowledge, while it has been reported[2] that pentavalent silicon derivatives obtained from benzyl alcoholates do give rise to allyl, benzyl or trimethysilyl anions which can be captured by electrophiles such as benzaldehyde or benzophenone.

In order to explore the reactivity and usefulness of the compounds prepared above, benzo[1,2]oxasiloles **1a–c** were transformed to **8a,b**, **9a,b** and **10a–c** (Scheme 4). Indeed homoallylic alcohols **8a**, where desilylation was achieved, were obtained by treatment with tetrabutylammonium fluoride (TBAF). Fluoride ion (KF) and hydrogen peroxide (H_2O_2) conditions[12] provided desilylated *ortho*-phenolic benzyl alcohols **9a,b**. Treatment of **1a–c** with methyllithium[13] (MeLi) resulted in nucleophilic methylation on silicon and opening of the Si–O bond to provide the silicon-containing homoallylic benzylic alcohols **10a–c**.

In all cases, the yields of the reactions were satisfactory and the compounds were obtained pure[14] by flash column chromatography.

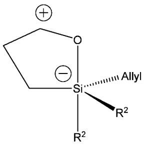
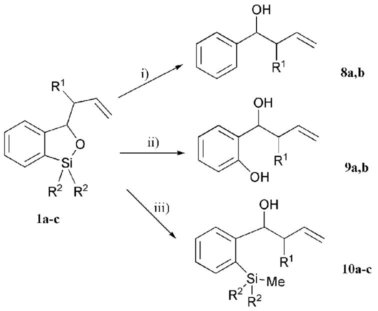


Fig. 2 Trigonal bipyramid pentavalent silicon.



Compound 1	Product	R¹	R²	Yield
1a	**8a**	H		79%
1b	**8b**	Me		77%
1c	**8a**	H		74%
1a	**9a**	H		61%
1b	**9b**	Me		68%
1c	**9a**	H		67%
1a	**10a**	H	Me	72%
1b	**10b**	Me	Me	63%
1c	**10c**	H	Allyl	72%

Scheme 4 Transformations of benzo[1,2]oxasiloles. i) TBAF, THF, ii) KF, H_2O_2 (Tamao conditions), iii) MeLi, Et_2O

In conclusion, we describe a novel rearrangement of a pentavalent silicon intermediate generated from *ortho*-allylsilyl benzaldehydes to provide 1,2-benzo[1,2]oxasiloles. The method accommodates substitution on the allylic moiety and proceeds in synthetically useful to excellent yields. The benzo[1,2]oxasiloles thus obtained can be further derivatized by various methods. A general method is also described for the preparation of the *ortho*-silyl benzaldehydes.

Notes and references

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