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Synthesis of a Key Reactive Unit for Use in the Divergent or Convergent Synthesis of Carbosilane Dendrimers

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Abstract: The new organosilane 4-triallylsilylphenol (**1**) can be synthesised in high yield *via* two routes using either 4-bromophenol or its silyl-group protected derivative as starting materials. Compound **1** can be used in the divergent or convergent synthesis of carbosilane dendrimers or conversely as a readily functionalisable dendrimer core unit. An improved synthesis of chlorotriallylsilane is also presented.

INTRODUCTION

The synthesis of dendrimers has expanded very rapidly in the last decade and these compounds are being investigated for a variety of diverse applications such as catalyst carriers, molecular probes, drug delivery media and other uses.[1] However, the widespread use of these new materials is hampered by the repetitive multi-step syntheses (*i.e.*, divergent syntheses) which are usually employed in dendrimer production.[1,2] This problem has been partially overcome by the convergent approach presented by Fréchet,[3a] in which small repeat units (*dendrons*) are coupled to a multifunctional core and hence large dendrimers can be assembled quickly.[1,3] A "one-pot" procedure, referred to as hyperbranched polymerisation, has also been presented for the synthesis of related (polydispersed) macromolecules.[4] We have studied the use of carbosilane dendrimers[5] as molecular frameworks for the attachment of catalytically active transition metal (TM) complexes.[6] These compounds have been used to demonstrate the feasibility of (homogeneous) catalyst recovery *via* ultrafiltration technology.[7] In this report we detail the synthesis of an organosilane unit that can be used as a versatile component for the attachment of molecular probes or TM complexes onto the dendrimer core (*cf.* artificial enzymes) or as a building block in the convergent *or* divergent synthesis of carbosilane dendrimers.

RESULTS AND DISCUSSION

The target compound for this work was the novel organosilane 4-triallylsilylphenol (**1**). Two synthetic approaches can be used to produce **1** but both require chlorotriallylsilane (**2**) as a reactant. Although this moisture-sensitive organosilane was synthesised over 40 years ago, published procedures involve the Grignard reaction of allylmagnesium chloride with $SiCl_4$, followed by vacuum distillation to separate **2** from other chlorosilanes (Yield ‹ 30%).[8] To avoid this difficult and tedious separation, the readily available triallylsilane (**3**) was used.[9] The reaction of **3** in acetonitrile solution at 70°C with an equimolar quantity of anhydrous $CuCl_2$ in the presence of excess Hünig's base, $EtN(i\text{-}Pr)_2$, afforded the desired chlorosilane **2** in 79% yield following pentane extraction and flash distillation (eq. 1).[10]

$$HSiCl_3 + 3\ H_2C{=}CHCH_2MgBr \rightarrow \underset{\mathbf{3}}{HSi(allyl)_3} + MgBrCl\downarrow$$

$$HSi(allyl)_3 + CuCl_2 \rightarrow \underset{\mathbf{2}}{ClSi(allyl)_3} + Cu\ salts\downarrow \qquad (1)$$

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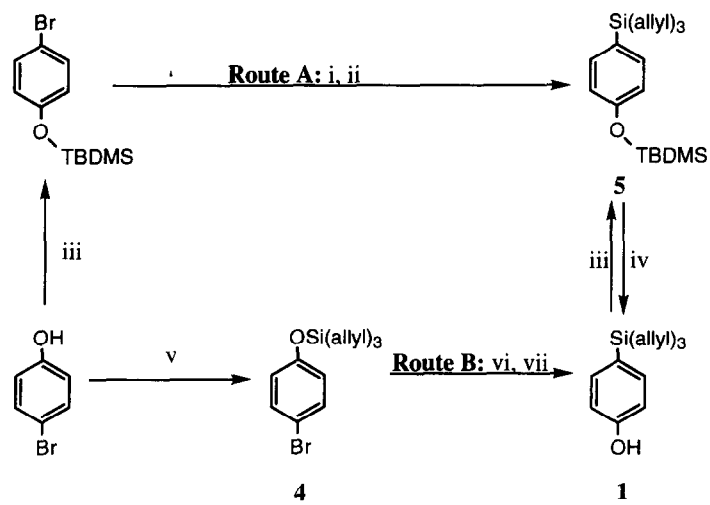
The two routes that were employed to synthesise the target phenol (**1**) involve either (**A**) addition of **2** to *in situ* produced 4-(*t*-butyldimethylsiloxy)phenyllithium, followed by deprotection of the alcohol functionality or (**B**) lithium-mediated silyl group migration of (4-bromophenyl)triallylsilyl ether (**4**).[11] Both routes are effective methods for the synthesis of **1**. Route **A** has the advantage that the protected phenol (**5**) is produced directly and thus can be used as a (protected) functionalisable core unit for further *divergent* dendritic growth. The second route (**B**) allows the direct synthesis of **1**, which can then be used in *convergent* dendrimer synthesis.

Method A: The treatment of a pentane solution of (4-bromophenyl)-*t*-butyldimethylsilyl ether[12,13] with 2.1 equiv. of *n*-BuLi at low temperature was followed by gradual heating of the mixture to room temperature. Volatile components were then removed and dry Et_2O added to dissolve the colourless powder. Cooling of this mixture to -78°C was followed by the addition of 1.2 mol equiv. of **2**. The solution was then warmed to ambient temperature. The product 4-(*t*-butyldimethylsiloxy)-(triallylsilyl)benzene (**5**) was then isolated in 46% yield by flash chromatography (3% EtOAc in hexanes). Deprotection of **5** was readily facilitated by the addition of a solution (THF) of *n*-Bu_4NF at 0°C to yield (24%) the desired phenol **1** (Scheme 1).[13,14]

Method B: The addition of two equiv. of *t*-BuLi to a solution of (4-bromophenyl)triallylsilyl ether (**4**)[15] at -78°C was followed by the addition of 10% aq. NH_4Cl at room temperature. Flash chromatographic separation (3% EtOAc/hexanes) of the oil obtained after solvent removal yielded compound **1** (81%).[13,14] Not surprisingly, **1** can then be readily converted to **5** by the reaction of the former with *t*-$BuMe_2SiCl$ (Scheme 1).

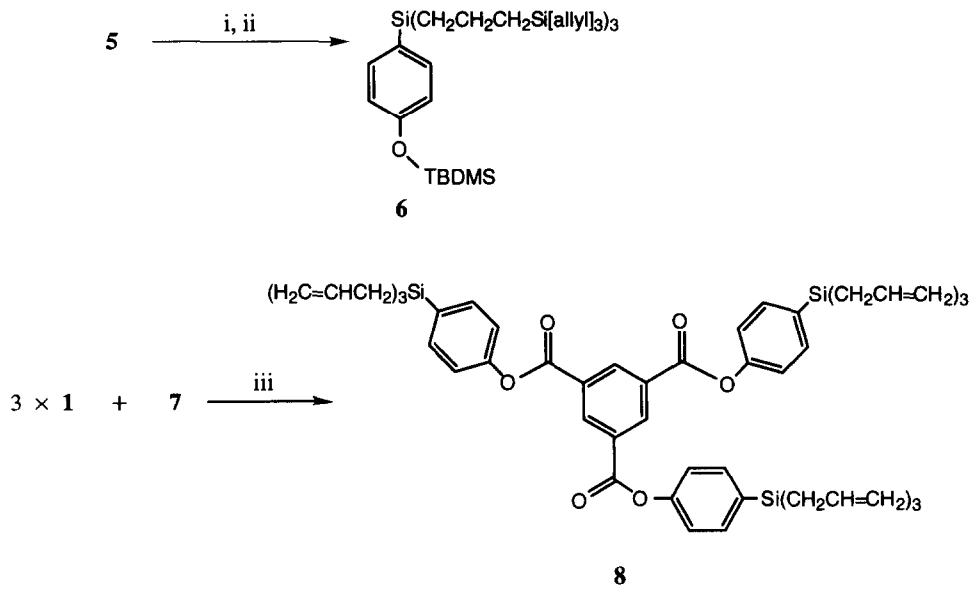


Scheme 1

(i). 2 × *n*-BuLi; (ii). 1.2 equiv. **2**; (iii). *t*-$BuMe_2SiCl$ / NEt_3
(iv). *n*-Bu_4NF / THF; (v). 1.2 equiv. **2** / NEt_3
(vi). 2 × *t*-BuLi; (vii). aq. NH_4Cl

The utility of **5** in carbosilane dendrimer synthesis is demonstrated by the first reaction depicted in Scheme 2. Thus, the $H_2PtCl_6 \cdot H_2O$ catalysed hydrosilation[16] of **5** with $HSiCl_3$, followed by reaction with 9 equiv. of allylmagnesium bromide (Et_2O) afforded dendron **6**.[13] This clearly demonstrates the utility of **5** as the initiation point for divergent carbosilane dendrimer synthesis. Deprotection of the alcohol functionality of **6** will allow for the attachment of catalytically active TM compounds or other groups (*i.e.*, **5** or **6** can also act as functionalisable core units).[17]

The synthetic versatility of **1** is further demonstrated by its use in the convergent synthesis of a carbosilane dendrimer. An example of this is shown in the second equation in Scheme 2. The dendritic ester **8** can be made simply by the reaction of **1** (3 equiv.) with 1,3,5-benzenetricarbonyl trichloride[18] (**7**; 1 equiv.) in THF in the presence of an organic base.[13]



Scheme 2

(i). $HSiCl_3$ / Pt (cat.); (ii). $H_2C{=}CHCH_2MgBr$
(iii). THF / NEt_3

CONCLUSIONS

The high yield synthesis of chlorotriallylsilane **2** has facilitated the availability of dendron **1**, which can be used as a functionalisable core unit (*via* reaction at the OH group) or as a reactive centre for convergent or divergent dendrimer synthesis. This represents the first report of a polyfunctional organosilicon compound for use in carbosilane macromolecular chemistry. Further use of these complexes in such synthesis is currently under study.

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10. ^{1}H NMR data for **2** (200 MHz, $CDCl_3$, 298 K, δ [ppm]): 5.80 (m, 3H, =C*H*), 5.00 (d, 6H, $^3J_{HH}$ = 12.4, C=CH_2), 1.88 (d, 6H, $^3J_{HH}$ = 7.9, CH_2Si).
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12. Prepared by the reaction of *t*-$BuMe_2SiCl$ and 4-bromophenol in C_6H_6 in the presence of excess NEt_3.
13. All new compounds gave satisfactory (C ± 0.4%; H ± 0.1%) elemental analyses.
14. ^{1}H NMR data for **5** (200 MHz, $CDCl_3$, 298 K, δ [ppm]): 7.38 (d, 2H, $^3J_{HH}$ = 8.2, Ar*H*), 6.85 (d, 2H, Ar*H*), 5.82 (m, 3H, =C*H*), 4.91 (m, 6H, =CH_2), 1.64 (d, 6H, d, $^3J_{HH}$ = 8.0, CH_2), 1.00 (s, 9H, CH_3), 0.22 (s, 6H, SiCH_3). Selected spectroscopic data for **1**; ^{1}H NMR (200 MHz, $CDCl_3$, 298K, δ [ppm]): 7.37 (d, 2H, $^3J_{HH}$ = 6.6 Hz, Ar*H*), 6.81 (d, 2H, Ar*H*), 5.81 (m, 3H, =C*H*), 4.90 (m, 6H, =CH_2), 3.19 (br, 1H, O*H*), 1.82 (d, 6H, $^3J_{HH}$ = 8.0 Hz, CH_2); IR (υ, cm^{-1}, CH_2Cl_2): 3576 (sh, OH), 3250 (br, OH [H-bonded]).
15. Synthesised by the addition of **2** to a solution (20% NEt_3 in C_6H_6) of 4-bromophenol followed by separation (flash chromatography: 3% EtOAc/hexanes as eluent).[13]
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