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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. © 1998 Elsevier Science Ltd. All rights reserved.

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]

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

$$\underset{\mathbf{3}}{HSi(allyl)_3} + CuCl_2 \rightarrow \underset{\mathbf{2}}{ClSi(allyl)_3} + Cu\ salts\downarrow \qquad (1)$$

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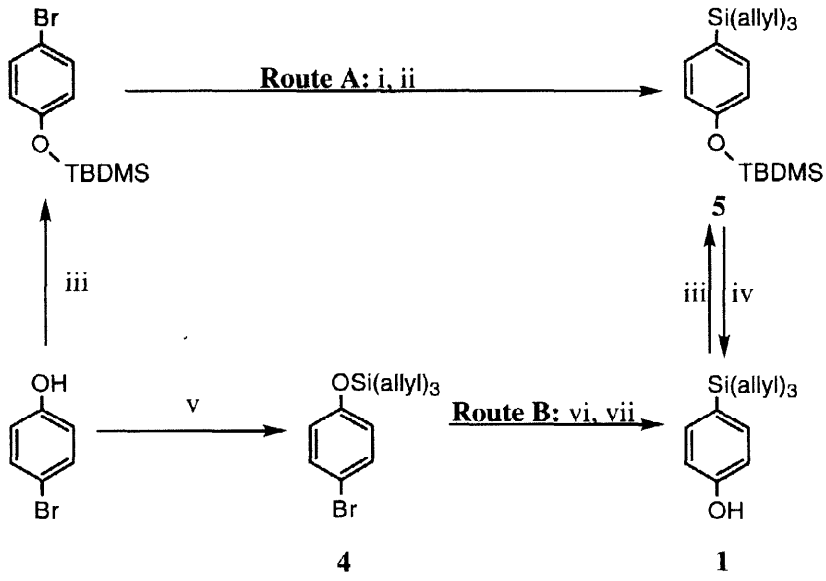
The two routes that were employed to synthesise the target phenol (**1**) involve either (**A**) addition of **2** to *in situ* produced 4-(*t*-butyldimethylsiloxy)phenyllithium, followed by deprotection of the alcohol functionality or (**B**) lithium-mediated silyl group migration of (4-bromophenyl)triallylsilyl 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).

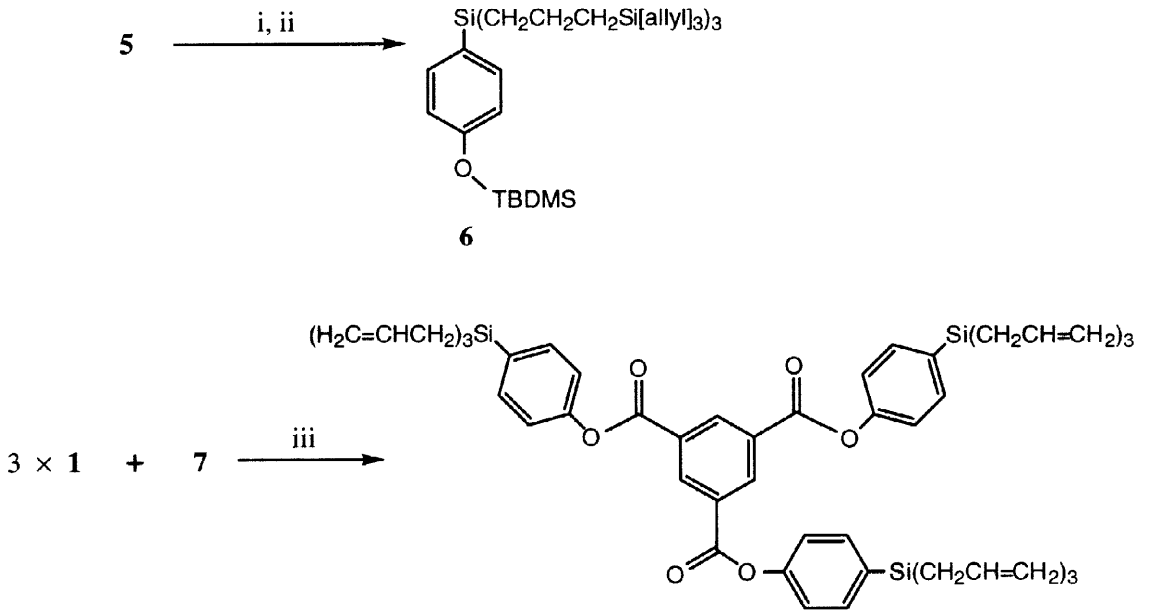


Scheme 1

(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$_2$SiCl 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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