# The Synthesis of Precisely Structured Polyurethanes. Part 1. Monomer Synthesis

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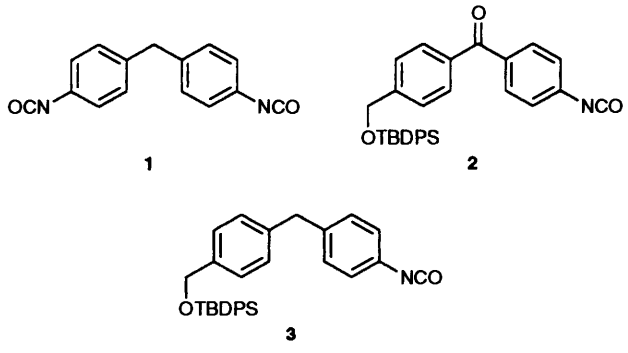
The synthesis of a series of bifunctional siloxymethyl isocyanate monomers, required for the solid phase synthesis of structurally defined polyurethane oligomers and copolymers is described. Thus, the MDI mimics **2**, **3** were synthesised *via* a desymmetrisation sequence from di-*p*-tolylmethanone and the *tert*-butyldiphenylsiloxymethylaryl isocyanates **19**, **22** and *tert*-butyldiphenylsiloxyethoxyethyl isocyanate **25**, an aliphatic variant, which were all synthesised from commercially available amino alcohols.

Polymers with precisely defined structures are of considerable potential industrial and academic importance.[1,2] It is one of the major goals of polymer synthesis to create known sequences of monomeric units in polymers with very narrow molecular weight distribution.[3] This enables the relationship between the polymer structure and its physical properties to be more accurately assessed, a process which is difficult to achieve with the dispersity of most common polymers including polyurethane ionomers,[4] and so allow the macroscopic properties to be created by molecular design.

We started from the premise that the solid-phase techniques, developed so successfully for peptide,[5-7] oligonucleotide[8,9] and other biopolymer[10-12] syntheses, could be applied to the synthesis of such structurally defined polyurethanes. This type of approach would be unlikely to be amenable to large scale synthesis, but could be invaluable in the preparation of speciality polymers and we now report the first steps towards achieving that goal.

The strategy is given in Scheme 1. In order to facilitate removal of the new oligomer, when assembled, solid-phase synthesis requires that an appropriate linker be placed between the resin and the growing chain. Attachment of the linker would then be followed by the stepwise addition of the urethane monomers to generate polyurethane oligomers of completely defined sequence and length, by a simple repetitive deprotect–couple procedure. As with biopolymer synthesis, any developing chains missed by the current monomer could be capped with an appropriate reagent.[13]

Unlike the standard butane-1,4-diol and 4,4′-methylenediphenyl diisocyanate (MDI) **1**, used typically in the commercial synthesis of polyurethanes, monomer units were required to incorporate both an isocyanate and a masked hydroxy group in the same molecule. For reasons of analogy to MDI **1** and perceived accessibility, the initial targets were the benzophenone **2** and its methylene analogue **3**.

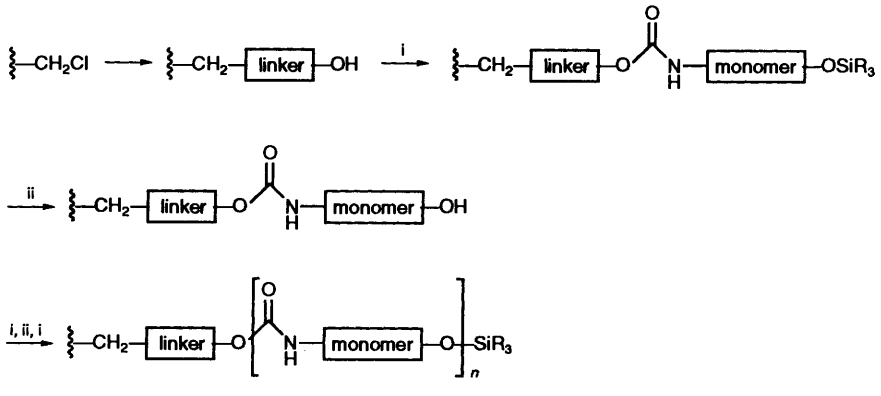



The monomers selected are unique in that a normally incompatible combination of functional groups (NCO and OH) are incorporated, so avoiding the need for the mixed aromatic di-isocyanate–aliphatic diol monomer system, and hence a more crystalline block should result.

After the required polymer length is assembled, the chain will be capped with a diisocyanate unit followed by linkage to the soft polyethyleneglycol block. Rational chain building of the next polyurethane block can then start from the new (polyethyleneglycol) hydroxy terminus. Suitable elastomeric properties would be expected with about a 50% w/w hard:soft segment ratio.

Finally, the completed chain could be cleaved from the solid support at the linker. A typical polyurethane oligomer, Fig. 1, prepared by the Merrifield technique, would have a regular structure as shown.

Somewhat surprisingly, the selected monomers, **2** and **3**, were unrecorded. Initial attempts to prepare these using palladium cross couplings and Friedel–Crafts technology were inefficient and alternative routes, using the commercially available 4,4′-dimethylbenzophenone (di-*p*-tolylmethanone), which contains




**Scheme 1** *Reagents:* i, OCN-monomer-$OSiR_3$; ii, $F^-$

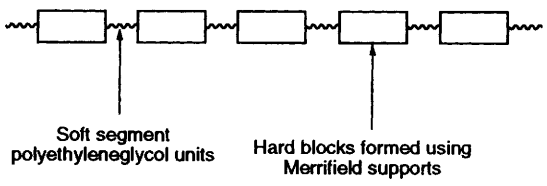
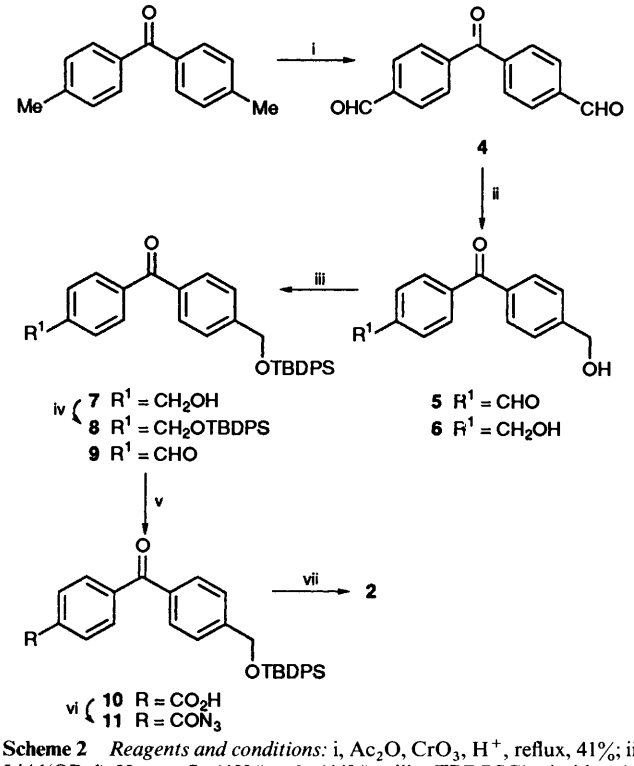



Fig. 1




**Scheme 2** *Reagents and conditions:* i, $Ac_2O$, $CrO_3$, $H^+$, reflux, 41%; ii, $LiAl(OBu^t)_3H$ ⟶ **5** (43%), **6** (44%); iii, TBDPSCl, imidazole, DMF ⟶ **7** (36%), **8** 21% from **6**, **9** (63%) from **5**; iv, $MnO_2$, 88%; v, $KMnO_4$, pH 4–5 ⟶ **10** (63%); vi, $(PhO)_2P(O)N_3$, $Et_3N$, 82%; vii, 80 °C, toluene

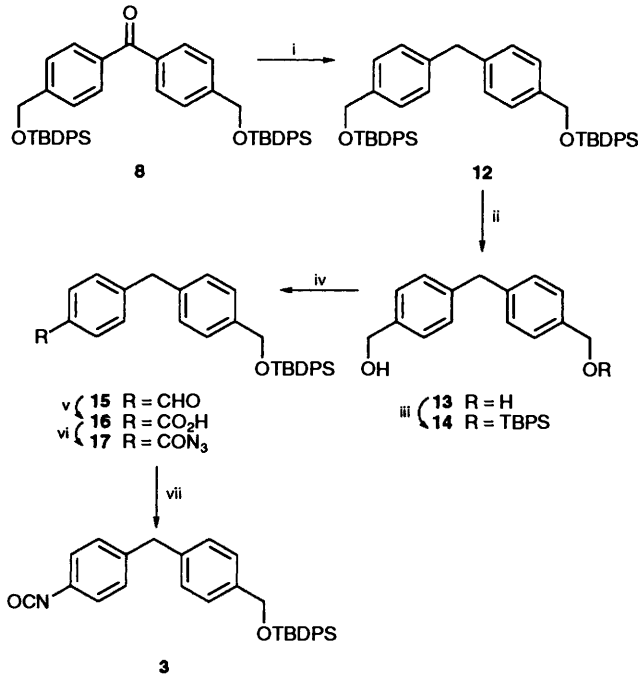
the required carbon skeleton, were then developed. The key process was the desymmetrisation of the molecule.

No reagent gave clean desymmetrisation. The oxidation of the terminal methyl groups was investigated using a range of reagents: ceric ammonium nitrate, potassium permanganate, chromyl chloride and chromium trioxide. Chromium trioxide gave the highest yield (41%) for the conversion of the starting material into the dialdehyde **4**. This aldehyde **4** could be reduced to a mixture of the mono alcohol **5** (43%) (and hence desymmetrised) and the diol **6** (44%), or it could be fully reduced to the triol. The former option was preferred because of the resulting desymmetrisation and lithium tri-*tert*-butoxyaluminium hydride proved to be the most selective reagent. The mono alcohol **5** so generated was then silylated with *tert*-butylchlorodiphenylsilane (TBDPSCl) to give the TBDPS-ether **9** (89%). The diol **6** was also semisilylated to generate a mixture of the diprotected diol **8** (21%) and monoprotected diol **7** (36%), together with residual unprotected diol. The monoprotected material **7** was readily oxidised to give the mono aldehyde **9** (89%). The residual diol was recycled and the disilylated material was used in the synthesis of the monomer **3** (see below).

The now desymmetrised molecule, the monoprotected aldehyde **9**, was further oxidised to the corresponding acid **10** (63%) using aqueous permanganate. The reaction time was varied in the range 5–20 min, but a longer reaction time led to desilylation and hence lower yields. The stepwise oxidation to the acid proved to be more efficient than the direct oxidation from the alcohol **7**. The acid was then readily converted into the azide **11** using diphenylphosphoryl azide (DPPA),[14] and, when heated at reflux in toluene, underwent a Curtius rearrangement to give the isocyanate **2**. The isocyanate **2** was highly water sensitive and so was not isolated prior to use, but was used directly in coupling reactions.[15] This route therefore gave access to the first target monomer, but it was apparent that, although compound **2** was a close structural mimic of MDI, there were two inherent problems: the high water sensitivity of the monomer, and the long synthetic route involved. Other monomers were therefore necessary.

The isocyanate **3**, the diphenylmethane analogue of compound **2**, was perceived be a less water sensitive, easier to handle and more accurate mimic of MDI.

Hence the disilylated side product **8**, generated during the preparation of compound **2**, was reduced to its methylene analogue **12** in quantitative yield using lithium aluminium hydride and aluminium chloride (Scheme 3). Attempts to

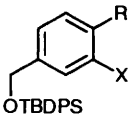



**Scheme 3** *Reagents and conditions:* i, $LiAlH_4$, $AlCl_3$, 100%; ii, TBAF ⟶ **13** (100%); iii, TBDPSCl, imidazole, DMF ⟶ **14** (41%), **12** (21%); iv, $MnO_2$ ⟶ **15** (61%); v, $KMnO_4$, pH 4–5 ⟶ **16** (65%); vi, DPPA, $Et_3N$ ⟶ **17** (92%); vii, 80 °C, toluene

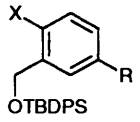
perform an analogous reduction on the diol **6** were not successful due to the lack of solubility in the solvent system used. The disilyl ether **12** was readily deprotected to generate the diol **13**, which was monoprotected to give compound **14** in 41% yield and then oxidised to give the aldehyde **15** in 61% yield, using manganese dioxide as before. Oxidation of the aldehyde **15** using aqueous permanganate gave the required acid **16** (65%) together with the keto-acid **10** (11%), which arose from overoxidation at the methylene position. Conversion of the acid into the azide **17** (92%) and then the isocyanate **18** was performed as before.

This monomer **3** was more stable to water and had a longer shelf-life than compound **2**. It proved to be a better monomer for the polymer synthesis but there still remained the inconveniently long synthesis. To improve the synthetic accessibiity of the monomers, MDI mimics were replaced by a range of simple monocyclic aryl monomers that could be synthesised using 2–3 steps. Initially, the protected isocyanate

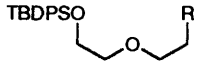
**19** was prepared in 48% overall yield from 4-aminobenzyl alcohol *via* silylation (to give compound **18**) and reaction with




**18** R = $NH_2$, X = H
**19** R = NCO, X = H
**20** R = $NH_2$, X = Br




**21** R = $NH_2$, X = H
**22** R = NCO, X = H
**23** R = $NH_2$, X = Br




**24** R = $NH_2$
**25** R = NCO

triphosgene. A brominated analogue **20** was readily prepared by bromination with NBS. The bromine atom is the focus for grafting of functionalised side chains by palladium coupling methods.[16] The 3-substituted isomer **22** was similarly synthesised from 3-aminobenzyl alcohol in 75% overall yield. This was also brominated, using NBS, to provide the bromo analogue **23** (24%).

All of the monomers described so far have an aromatic core and would be expected to form the 'hard', rigid blocks when assembled. A monomer **25**, for the preparation of structurally defined 'soft' blocks was also prepared from 2-(2-aminoethoxy)-ethanol. Protection of the aminoethanol as the TBDPS ether **24** was achieved in quantitative yield in the absence of solvent. Conversion of the amine into the isocyanate was more problematical. The addition of a tertiary base was necessary to depolymerise the triphosgene *in situ*. A range of these: triethylamine (28%); pyridine (0%); DBU (0%); 2,6-di-*tert*-butyl-4-methylpyridine (0%); Hunigs base (43%) and DMAP (46%), was used. The use of diphosgene, gave no improvement. The highest yield (48%) was finally obtained using triphosgene–DMAP in refluxing dichloromethane with slow addition of the amine **24**.

We now had available a collection of five siloxymethyl(aryl or alkyl) isocyanate monomer units and were in a position to apply these to the solid-phase synthesis of a variety of hard block oligomeric polyurethanes. This will be the topic of the next paper in the series.

## Experimental

Mps were carried out on a Kofler hot stage and are uncorrected; IR spectra were recorded on Perkin-Elmer 1700 FT spectrometer; $^1$H NMR spectra on a Bruker WH-250 FT (250 MHz), GE-300 FT (300 MHz), JEOL GSX FT (270 MHz—with a GSX data system) or Varian 60 MHz spectrometer. Chemical shifts ($\delta$) are reported in ppm relative to residual undeuteriated solvent, *i.e.* $\delta$ 7.26 for chloroform and 7.37 for benzene and $J$ values are given in Hz. $^{13}$C NMR spectra were recorded on the Bruker and JEOL instruments, with chemical shifts reported against $CDCl_3$ reference.

Unless otherwise stated, petroleum refers to light petroleum, bp 40–60 °C, which was redistilled before use. Column chromatography was carried out using Silica gel H. For reactions under anhydrous conditions, THF and diethyl ether were pre-dried with sodium metal and then distilled from sodium–benzophenone immediately before use. Other reagents were purified according to literature methods.[17] Where stated, aqueous work-up refers to a sequential water and brine wash, followed by drying of the organic solution over anhydrous magnesium sulfate, filtering and then removal of the solvents under reduced pressure.

*Bis*(4-*formylphenyl*) *Ketone* **4**.—Conc. sulfuric acid (12 cm$^3$) was added dropwise to a stirred solution of di-*p*-tolylmethanone (6.0 g, 28.6 mmol) in acetic anhydride (60 cm$^3$, 0.642 mol), at 0 °C. To this was added dropwise a solution of chromium trioxide (15.9 g, 0.159 mol) in acetic anhydride (70 cm$^3$), at such a rate that the temperature did not exceed 10 °C. After all the chromium trioxide had been added, stirring was continued at room temperature for a further 2 h. The reaction mixture was added to an ice–water mixture (300 cm$^3$) and the solid was collected by filtration. Further material was extracted from the solution with diethyl ether (2 × 100 cm$^3$); the ethereal extracts were dried and evaporated. The combined solid products were washed with 2% aqueous sodium carbonate (1 × 100 cm$^3$) and then heated at reflux in ethanol–water–conc. sulfuric acid (105 cm$^3$, 10 : 10 : 1) for 30 min. The solution was cooled to room temperature and the product was extracted into ethyl acetate (4 × 100 cm$^3$) and the combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate (2 × 100 cm$^3$), dried, and evaporated to yield the crude product. This was purified by flash chromatography (diethyl ether–hexane, gradient 30–100%) to give the *benzophenone* **4** (2.79 g, 41%), as a cream solid. Alternatively, the product could be purified by recrystallisation to a constant mp, 150–151 °C (chloroform); $\nu_{max}$(Nujol)/cm$^{-1}$ 2930s, 1705m and 1654m; $\delta_H$(270 MHz; $CDCl_3$) 7.93 (4 H, d, $J$ 7.9, 3-H), 8.02 (4 H, d, $J$ 7.9, 2-H) and 10.13 (2 H, s, CHO); $\delta_C$(125 MHz; $CDCl_3$) 129.61 (C-3), 130.37 (C-2), 138.93 (C-4), 141.49 (C-1), 191.35 (CHO) and 194.89 (C=O); *m/z* (EI) 238 ($M^+$, 46%), 133 ($M^+ - C_6H_5CHO$, 100), 119 ($C_8H_7O^+$, 64), 105 ($C_7H_5O^+$, 36) and 77 ($Ph^+$, 40) (Found: $M^+$ 238.0631. $C_{15}H_{10}O_3$ requires $M$ 238.0630).

4-*Formylphenyl* (4-*Hydroxymethyl*)*phenyl Ketone* **5** *and Bis*[(4-*hydroxymethyl*)*phenyl*] *Ketone* **6**.—Lithium tri-*tert*-butoxyaluminium hydride (56 mg, 0.22 mmol) was added at 0 °C to a solution of the dialdehyde **4** (53 mg, 0.22 mmol) in dry THF (10 cm$^3$). Stirring was continued at 0 °C for 2 h and then a further portion of reductant (24 mg, 0.094 mmol) was added. The reaction mixture was warmed to room temperature and stirred for a further 18 h, after which 10% hydrochloric acid (5 cm$^3$) was added. The reaction products were extracted into ethyl acetate (3 × 20 cm$^3$) and the combined extracts washed with brine (1 × 20 cm$^3$), dried and evaporated. Purification by flash chromatography (ethyl acetate–hexane, gradient 50–100%) first yielded the *benzyl alcohol* **5** (24 mg, 43%) as a pale cream solid, mp 118–119 °C (chloroform); $\nu_{max}$(Nujol)/cm$^{-1}$ 3406br, 2923s, 2850m, 1700s, 1650m and 1600s; $\delta_H$(270 MHz; $CDCl_3$) 4.80 (2 H, s, $CH_2OH$), 7.49 (2 H, d, $J$ 6.6, 3-H), 7.77 (2 H, d, $J$ 6.6, 2-H), 7.88 (2 H, d, $J$ 6.6, 3'-H), 7.98 (2 H, d, $J$ 6.6, 2'-H) and 10.11 (1 H, s, CHO); $\delta_C$(125 MHz; $CDCl_3$) 64.52 ($CH_2$), 126.55 (C-2), 129.46 (C-3'), 130.22 (C-3), 130.39 (C-2'), 135.88 (C-4), 138.47 (C-4'), 142.64 (C-1'), 146.37 (C-1), 191.56 (CHO) and 195.45 (C=O); *m/z* (EI) 240 ($M^+$, 55%), 238 ($M^+ - 2$ H, 15), 211 ($M^+$ – CHO, 16), 135 ($M^+ - C_6H_4CHO$, 100), 133 ($M^+ - C_6H_5CH_2OH$, 65) and 105 ($C_7H_5O^+$, 27) (Found: $M^+$ 240.0784. $C_{15}H_{12}O_3$ requires $M$ 240.0786).

Further elution gave the *benzophenone* **6** (25 mg, 44%) as a white solid, mp 129–130 °C (ethyl acetate); $\nu_{max}$(Nujol)/cm$^{-1}$ 3226br, 2930s, 1645m, 1608w and 1571s; $\delta_H$(270 MHz; $CDCl_3$) 1.81 (2 H, t, $J$ 5.9, $CH_2OH$), 4.81 (4 H, d, $J$ 5.6, $CH_2OH$), 7.50 (4 H, d, $J$ 8.0, 3-H, 5-H) and 7.81 (4 H, d, $J$ 8.0, 2-H, 6-H); $\delta_C$(125 MHz; $CDCl_3$) 63.73 ($CH_2$), 126.20 (C-3), 130.07 (C-2), 136.32 (C-1), 146.17 (C-4) and 196.88 (C=O); *m/z* (EI) 242 ($M^+$, 83%), 240 ($M^+ - 2$ H, 12), 213 ($M^+$ – CHO, 18) and 211 ($M^+ - CH_2OH$, 28) (Found: $M^+$ 242.095. $C_{15}H_{14}O_3$ requires $M$ 242.094).

4-(tert-*Butyldiphenylsiloxymethyl*)*phenyl* 4-(*Hydroxymethyl*)*phenyl Ketone* **7** *and Bis*(4-tert-*butyldiphenylsiloxymethyl*)-*phenyl Ketone* **8**.—Imidazole (1.84 g, 27.1 mmol) and *tert*-butylchlorodiphenylsilane (1.97 cm$^3$, 7.58 mmol) were added to a solution of the diol **6** (2.62 g, 10.8 mmol) in dry DMF (5 cm$^3$) at 0 °C. The reaction mixture was stirred at room temperature

for 18 h, water (30 $cm^3$) was added and the product was extracted with diethyl ether (3 × 50 $cm^3$). The combined organic extracts were washed with brine (50 $cm^3$), dried and evaporated. The product was purified by flash chromatography (ethyl acetate–hexane, gradient 20–100%) first to yield the *disilylated benzophenone* **8** (1.61 g, 21%) as a colourless oil, $\nu_{max}$(film)/$cm^{-1}$ 2930s, 1738s, 1651s, 1614s and 1470s; $\delta_H$(270 MHz; $CDCl_3$) 1.11 (6 H, s, Me), 1.17 (6 H, s, Me), 1.18 (6 H, s, Me), 4.90 (4 H, s, $CH_2OSi$), 7.44 (16 H, m, Ar) and 7.77 (12 H, m, Ar); $\delta_C$(100 MHz; $CDCl_3$) 19.29 ($CMe_3$), 26.46 (Me), 26.54 (Me), 26.83 (Me), 65.14 ($CH_2OSi$), 125.54 (C-3), 127.77 (C-3′), 129.79 (C-4′), 130.17 (C-2), 133.19 (C-1′), 135.14 (C-2′), 136.37 (C-1), 145.75 (C-4) and 196.31 (C=O); *m/z* (EI) 719 ($M^+$ + 1, 40%), 718 ($M^+$, 26), 373 ($M^+$ − $C_6H_4CH_2OTBDPS$, 19), 199 ($HOSiPh_2^+$, 50) and 135 ($C_8H_5O_2^+$, 100) (Found: $M^+$ 718.3294. $C_{47}H_{50}O_3Si_2$ requires *M*, 718.3299).

Further elution gave the *monosilylated benzophenone* **7** (1.89 g, 36%), as a colourless oil, $\nu_{max}$(film)/$cm^{-1}$ 3456br, 2932s, 1739m, 1700m, 1657s, 1609s and 1572m; $\delta_H$(270 MHz; $CDCl_3$) 1.19 (9 H, s, $Bu^t$), 4.78 (2 H, s, $CH_2OH$), 4.92 (2 H, s, $CH_2OSi$), 7.45 (8 H, m, Ar) and 7.80 (10 H, m, Ar); $\delta_C$(125 MHz; $CDCl_3$) 19.30 ($CMe_3$), 26.78 ($CMe_3$), 64.60 ($CH_2OH$), 65.10 ($CH_2OSi$), 125.55 and 126.35 (C-3, C-3′), 127.75 (C-3″), 129.79 (C-4″), 130.13 and 130.31 (C-2, C-2′), 133.10 (C-1″), 135.49 (C-2″), 136.10 and 136.95 (C-1, C-1′), 145.30 and 145.95 (C-4, C-4′) and 196.05 (C=O); *m/z* (EI) 479 ($M^+$ − H, 1%), 465 ($M^+$ − Me, 1), 423 ($M^+$ − $Bu^t$, 50) and 135 ($C_8H_7O_2^+$, 100).

Finally, unchanged starting diol **6** (646 mg, 25%) was eluted.

4-(tert-*Butyldiphenylsiloxymethyl*)*phenyl* 4′-*Formylphenyl Ketone* **9**.—*Method 1*. Activated manganese dioxide (5.67 g, 65.2 mmol) was added to a solution of the mono alcohol **7** (2.09 g, 4.35 mmol) in chloroform (40 $cm^3$) and stirred at room temperature for 18 h. The material was filtered through Celite and the Celite was washed with diethyl ether (100 $cm^3$). The combined ethereal extracts were evaporated to yield the pure *silyl ether* **9** (1.86 g, 89%) as a clear oil; $\nu_{max}$(film)/$cm^{-1}$ 2931s, 2739m, 1708s, 1658s, 1608s, 1590m and 1500s; $\delta_H$(270 MHz; $CDCl_3$) 1.14 (9 H, s, $Bu^t$), 4.88 (2 H, s, $CH_2OSi$), 7.47 (10 H, m, Ar), 7.71 (4 H, m, Ar), 7.93 (2 H, d, *J* 8.1, 2′-H), 8.01 (2 H, d, *J* 8.1, 3′-H) and 10.1 (1 H, s, CHO); $\delta_C$(125 MHz; $CDCl_3$) 19.25 ($CMe_3$), 21.25 ($CMe_3$), 65.07 ($CH_2$), 125.79 (C-3), 127.75 (C-3″), 129.39 (C-3′), 129.80 (C-4″), 130.15 and 130.21 (C-2, C-2′), 133.10 (C-1″), 135.45 (C-2″), 135.33 (C-1), 138.34 (C-4′), 142.78 (C-1′), 146.74 (C-4), 191.55 (CHO) and 195.45 (C=O); *m/z* (EI) 421 ($M^+$ − $Bu^t$, 84%), 391 ($M^+$ − $Bu^t$ − CHOH, 20), 343 ($M^+$ − $Bu^t$ − Ph, 15) and 199 ($HOSiPh_2^+$, 100) (Found: $M^+$ − $Bu^t$, 421.1260. $C_{27}H_{21}O_3Si$ requires *M* 421.1260).

*Method 2*. Imidazole (1.89 g, 27.8 mmol) and *tert*-butylchlorodiphenylsilane (2.0 $cm^3$, 7.70 mmol) were added to a solution of the hydroxy aldehyde **6** (2.21 g, 9.21 mmol) in dry DMF (10 $cm^3$) at 0 °C. The reaction mixture was stirred at room temperature for 18 h and then water (30 $cm^3$) was added and the product was extracted with diethyl ether (3 × 70 $cm^3$). The combined organic extracts were washed with brine (1 × 50 $cm^3$), dried and evaporated. The product was purified by flash chromatography (ethyl acetate–hexane, 1:5) to yield the *silyl ether* **9** (2.78 g, 63%) identical with the above material.

4-[4′-(tert-*Butyldiphenylsiloxymethyl*)*phenylcarbonyl*]-*benzoic Acid* **10**.—Aqueous sodium dihydrogen phosphate (5%, 20 $cm^3$) was added to a solution of the formyl ketone **9** (1.56 g, 3.26 mmol) in 2,2-dimethylpropanol (20 $cm^3$) and the pH of the resulting solution was adjusted to 4–5, using 10% dilute hydrochloric acid. Potassium permanganate (3.10 g, 19.5 mmol; in 20 $cm^3$ water) was added and the mixture was stirred at room temperature for 5 min. Sat. sodium sulfite (40 $cm^3$) was added and the solution was adjusted to pH 3 by the addition of 10% hydrochloric acid. The product was extracted with ethyl acetate (3 × 50 $cm^3$) and the combined extracts were washed with brine, dried and evaporated. The residue was purified by flash chromatography (ethyl acetate–hexane, 3:7) to yield the pure *carboxylic acid* **10** (1.01 g, 63%) as colourless crystals, mp 160–161 °C (ethyl acetate); $\nu_{max}$(film)/$cm^{-1}$ 3500br, 2921s, 1690m, 1650m, 1600w and 1510w; $\delta_H$(270 MHz; $CDCl_3$) 1.14 (9 H, s, $Bu^t$), 4.88 (2 H, s, $CH_2OSi$), 7.45 (8 H, m, Ar), 7.82 (8 H, m, Ar) and 8.26 (2 H, d, *J* 8.2, 2,6-H); $\delta_C$(125 MHz; $CDCl_3$) 19.34 ($CMe_3$), 26.86 (2 × Me), 27.02 (1 × Me), 65.14 ($CH_2$), 125.83 (C-3′), 127.82 (C-3″), 129.80 (C-4″), 129.90, 130.13 and 130.29 (C-3, C-2 and C-2′), 132.12 (C-1), 133.19 (C-1″), 135.50 (C-1′), 135.55 (C-2″), 142.47 (C-4), 146.74 (C-4′), 170.60 ($CO_2H$) and 195.67 (C=O); *m/z* (EI) 451 ($M^+$ + H − $CO_2$, 37%), ($M^+$ − $Bu^t$, 12), 199 ($HOSiPh_2^+$, 19) and 149 ($C_8H_5O_3^+$, 100) (Found: C, 72.0; H, 5.7. $C_{31}H_{30}O_4Si{\cdot}H_2O$ requires C, 72.63; H, 6.29%).

4′-(*Azidocarbonyl*)*phenyl* 4-(tert-*Butyldiphenylsiloxymethyl*)-*phenyl Ketone* **11**.—Diphenylphosphoryl azide (190 mg, 0.328 mmol) and triethylamine (0.5 $cm^3$) were added to a solution of the acid **10** (135 mg, 0.273 mmol) in dry THF (10 $cm^3$). The reaction mixture was stirred at room temperature for 18 h, filtered through basic alumina and evaporated to yield the *azide* **11** (116 mg, 82%) as a clear oil, which was used without further purification; $\nu_{max}$(film)/$cm^{-1}$ 3460br, 2931s, 2182s, 2136s, 1694s, 1625s, 1609s, 1590m and 1501m; $\delta_H$(270 MHz; $CDCl_3$) 1.13 (9 H, s, $Bu^t$), 4.86 (2 H, s, $CH_2OSi$), 7.43 (8 H, m, Ar), 7.78 (8 H, m, Ar) and 8.15 (2 H, d, *J* 6.7, 3′-H); *m/z* (EI) ($M^+$ − $C_8H_5O_3$, 57) and 199 ($HOSiPh_2^+$, 100).

4-(tert-*Butyldiphenylsiloxymethyl*)*phenyl* 4′-*Isocyanatophenyl Ketone* **2**.—The azide **11** (116 mg, 0.224 mmol) was heated at 80 °C for 2 h in dry toluene (10 $cm^3$) and then cooled to room temperature. TLC and NMR analysis indicated complete conversion of the azide into the isocyanate **2**; $\nu_{max}$(film)/$cm^{-1}$ 2930s, 2171s, 1590m, 1500s and 1440m; $\delta_H$(270 MHz; $CDCl_3$) 1.18 (9 H, s, $Bu^t$), 4.85 (2 H, s, $CH_2OSi$), 7.47 (10 H, m, Ar) and 7.76 (8 H, m, Ar). The crude isocyanate **2** was used immediately for coupling.

*Bis*(tert-*butyldiphenylsilyl*) 4,4′-*Methylenedibenzyl Ether* **12**.—Aluminium chloride (274 mg, 1.98 mmol) in diethyl ether (20 $cm^3$) was added dropwise to a solution of lithium aluminium hydride (75 mg, 1.98 mmol) in dry diethyl ether (20 $cm^3$) and the solution was stirred for 5 min. To this was added, *via* a cannula, a solution of the benzophenone **8** (1.42 g, 1.98 mmol) in diethyl ether (30 $cm^3$) at such a rate as to maintain a gentle reflux. The mixture was stirred for a further 2 h at room temperature and then water (2 $cm^3$), sodium hydroxide (10%, 2 $cm^3$) and finally water (2 $cm^3$) were added. The mixture was dried, filtered through magnesium sulfate and evaporated to yield the pure *diphenylmethane* **12** (1.40 g, 100%) as a colourless oil; $\nu_{max}$(film)/$cm^{-1}$ 2930s, 1510w, 1450m and 1428s; $\delta_H$(270 MHz; $CDCl_3$) 1.16 (9 H, s, $Bu^t$), 4.04 (2 H, s, $CH_2Ar_2$), 4.82 (4 H, s, $CH_2OSi$), 7.24 (4 H, d, *J* 7.8, 3,5-H), 7.35 (4 H, d, *J* 7.8, 2,6-H), 7.45 (4 H, m, Ar) and 7.78 (6 H, m, Ar); $\delta_C$(125 MHz; $CDCl_3$) 19.32 ($CMe_3$), 26.57 (Me), 26.87 (2 × Me), 41.37 ($CH_2Ar_2$), 65.40 ($CH_2OSi$), 126.19 (C-2), 127.68 (C-3′), 128.74 (C-3), 129.64 (C-4′), 133.60 (C-1′), 135.58 (C-2′), 138.81 (C-4) and 139.84 (C-1); *m/z* (FAB) 704 ($M^+$, 10%), 703 ($M^+$ − H, 15), 199 ($HOSiPh_2^+$, 70) and 135 ($C_8H_5O_2^+$, 100) (Found: $M^+$ − 1, 703.3446. $C_{47}H_{52}O_2Si_2$ requires *M*, 703.3438).

4,4′-*Methylenedibenzyl Alcohol* **13**.—TBAF (5.70 $cm^3$, 5.70 mmol; 1 mol $dm^{-3}$ solution in THF) was added dropwise to a solution of the siloxylated diphenylmethane **12** (2.00 g, 2.84 mmol) in dry THF (10 $cm^3$). The reaction mixture was stirred at room temperature for 18 h. Water (50 $cm^3$) was added and the

product was extracted into ethyl acetate (3 × 60 $cm^3$). The combined organic extracts were dried and evaporated, hexane (50 $cm^3$) was added and the solution was filtered through a pad of silica. The silica was washed with hexane (100 $cm^3$), followed, separately, by ethyl acetate. The ethyl acetate was removed under reduced pressure to give the diol **13** (650 mg, 100%) as colourless crystals, mp 118–119 °C (ethyl acetate); $\nu_{max}$(Nujol)/$cm^{-1}$ 3300br, 2919s, 1600w and 1510w; $\delta_H$(270 MHz; $CDCl_3$) 3.96 (2 H, s, $CH_2Ar_2$), 4.59 (4 H, s, $CH_2OH$), 7.19 (4 H, d, *J* 8.1, 3,3′,5,5′-H) and 7.29 (4 H, d, *J* 8.1, 2,2′,6,6′-H); $\delta_C$(125 MHz; $CDCl_3$) 42.16 ($CH_2Ar_2$), 65.03 ($CH_2OH$), 128.23 (C-2′), 129.85 (C-3′), 140.32 (C-4′) and 141.80 (C-1′); *m*/*z* (EI) 228 ($M^+$, 87%), 197 ($M^+ - CH_2OH$, 100), 179 ($M^+ - CH_2OH - H_2O$, 29), 165 ($M^+ - 2$ ($CH_2OH$) − H, 37), 104 ($CH_2C_6H_4CH_2^+$, 52) and 91 ($PhCH_2^+$, 46) (Found: C, 79.2; H, 6.9; $M^+$, 228.1149. $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.0%; *M*, 228.1150).

4-[4-(tert-*Butyldiphenylsiloxymethyl*)*phenylmethyl*]*benzyl Alcohol* **14**.—The reaction was carried out as above for the keto-analogue **7**, with imidazole (298 mg, 4.38 mmol), *tert*-butylchlorodiphenylsilane (0.32 $cm^3$, 1.22 mmol) and the diol **13** (482 mg, 1.75 mmol) in dry DMF (5 $cm^3$). The reaction mixture was worked up as before and purified by flash chromatography (ethyl acetate–petroleum, gradient, 20–100%) firstly to yield the diether **12** (259 mg, 21%), identical with the material obtained previously. Further elution gave the title *alcohol* **14** (335 mg, 41%) as a colourless oil; $\nu_{max}$(film)/$cm^{-1}$ 3332br, 2930s, 1600w, 1589w and 1513s; $\delta_H$(270 MHz; $CDCl_3$) 1.10 (9 H, s, $Bu^t$), 3.99 (2 H, s, $CH_2Ar_2$), 4.67 (2 H, s, $CH_2OH$), 4.75 (2 H, s, $CH_2OSi$), 7.29 (14 H, m, Ar) and 7.69 (4 H, m, Ar); $\delta_C$(125 MHz; $CDCl_3$) 19.32 ($CMe_3$), 26.86 (3 × Me), 41.36 ($CH_2Ar$), 65.23 ($CH_2OH$), 65.37 ($CH_2OSi$), 126.22 and 127.26 (C-2, C-3′), 127.68 (C-3″), 128.70 and 129.14 (C-3, C-2′), 129.64 (C-4″), 133.60 (C-1″), 135.59 (C-2″), 138.67 and 138.91 (C-1, C-4′) and 139.61 and 140.82 (C-4, C-1′); *m*/*z* (FAB) 465 ($M^+$ − H, 29%), 449 ($M^+ - OH$, 11), 211 ($M^+ + H - OTBDPS$, 100), 199 ($HOSiPh_2^+$, 46), and 135 ($C_8H_7O_2^+$, 100) (Found: $M^+ - 1$, 465.2254. $C_{31}H_{34}O_2Si$ requires *M*, 465.2250).

Finally, the starting diol **13** (39 mg, 8%), $R_f$ 0.22 (diethyl ether–hexane) was eluted.

4-[4′-(tert-*Butyldiphenylsiloxymethyl*)*phenylmethyl*]*benzaldehyde* **15**.—The reaction was carried out as above for the keto-analogue **7**, with activated manganese dioxide (1.70 g, 19.5 mmol) and the mono alcohol **14** (700 mg, 19.5 mmol) in chloroform (20 $cm^3$) to yield the aldehyde **15** (425 mg, 61%) as a clear oil, $R_f$ 0.50 (diethyl ether–hexane, 1:1); $\nu_{max}$(film)/$cm^{-1}$ 2929s, 1694s, 1606s, 1508s, 1514s, 1471m and 1428s; $\delta_H$(270 MHz; $CDCl_3$) 1.14 (9 H, s, $Bu^t$), 4.08 (2 H, s, $CH_2Ar_2$), 4.80 (2 H, s, $CH_2OSi$), 7.19 (2 H, d, *J* 8.3, 2,6-H), 7.40 (10 H, m, Ar), 7.75 (4 H, m, Ar), 7.83 (2 H, d, *J* 8.3, 2-H) and 10.0 (1 H, s, CHO); $\delta_C$(125 MHz; $CDCl_3$) 19.31 ($CMe_3$), 26.85 ($CMe_3$), 41.81 ($CH_2Ar_2$), 65.28 ($CH_2OSi$), 126.39 (C-3′), 127.69 (C-3″), 128.80 (C-2′), 129.55 (C-2), 129.68 (C-4″), 130.02 (C-3), 130.18 (C-1′), 133.50 (C-1″), 135.57 (C-2″), 138.30 (C-1), 139.38 (C-4), 148.57 (C-4′) and 191.92 (CHO); *m*/*z* (FAB) 464 ($M^+$, 22%), 463 ($M^+$ − H, 34), 407 ($M^+ - Bu^t$, 25), 209 ($M^+$ − OTBDPS, 100), 199 ($HOSiPh_2^+$, 72) and 135 ($C_8H_7O_2^+$, 97) (Found: $M^+$, 464.2184. $C_{31}H_{32}O_2Si$ requires *M*, 464.2172).

4-[4′-(tert-*Butyldiphenylsiloxymethyl*)*phenylmethyl*]*benzoic Acid* **16**.—The reaction was carried out as above for the keto analogue **9**, with the aldehyde **15** (500 mg, 1.10 mmol) in 2,2-dimethylpropanol (6 $cm^3$), sodium dihydrogen phosphate (5%, 3 $cm^3$), and potassium permanganate (348 mg, 1.10 mmol; in 3 $cm^3$ water). The product was purified by flash chromatography (ether–hexane gradient, 50–100%) to yield the acid **16** (343 mg, 65%); $\nu_{max}$(film)/$cm^{-1}$ 3422br, 2930m, 1689s and 1600w; $\delta_H$(270 MHz; $CDCl_3$) 1.16 (9 H, s, $Bu^t$), 4.10 (2 H, s, $CH_2Ar_2$), 4.80 (2 H, s, $CH_2OSi$), 7.20 (2 H, d, *J* 8.1, 3,5-H), 7.42 (10 H, m, Ar), 7.76 (4 H, m, Ar) and 8.10 (2 H, d, *J* 8.3, 2,6-H); *m*/*z* (FAB) 480 ($M^+$, 20%), 479 ($M^+$ − H, 41), 423 ($M^+ - Bu^t$, 27), 225 ($M^+$ − OTBDPS, 100), 199 ($HOSiPh_2^+$, 63) and 135 ($C_8H_7O_2^+$, 82) (Found: $M^+ - 1$, 479.2073. $C_{31}H_{31}O_3Si$ requires *M*, 479.2043).

Further elution gave the keto acid **10** (60 mg, 11%), identical with the material obtained previously.

4-[4′-(tert-*Butyldiphenylsiloxymethyl*)*phenylmethyl*]*benzoyl Azide* **17**.—The reaction was carried out as above for the keto-analogue **11** with diphenylphosphoryl azide (153 mg, 0.623 mmol), triethylamine (0.5 $cm^3$) and the acid **16** (243 mg, 0.566 mmol) in dichloromethane (10 $cm^3$) to yield the *azide* **17** (237 mg, 92%) as a clear oil, which was used without further purification, $R_f$ 0.70 (diethyl ether–hexane, 1:1); $\nu_{max}$(film)/$cm^{-1}$ 2930s, 2174s, 1692s and 1606s; $\delta_H$(270 MHz; $CDCl_3$) 1.10 (9 H, s, $Bu^t$), 4.09 (2 H, s, $CH_2Ar_2$), 4.82 (2 H, s, $CH_2OSi$), 7.18 (2 H, d, *J* 8.4, 3,5-H), 7.40 (10 H, m, Ar), 7.78 (4 H, m, Ar) and 8.10 (2 H, d, *J* 8.4, 2,6-H).

4-[4′-(tert-*Butyldiphenylsiloxymethyl*)*phenylmethyl*]*phenyl Isocyanate* **3**.—The azide **17** (237 mg, 0.467 mmol) was heated at 80 °C for 2 h in toluene (10 $cm^3$) and then cooled to room temperature. TLC analysis indicated complete conversion of the azide into the *isocyanate* **3**, $R_f$ 0.35 (diethyl ether–hexane, 1:1); $\nu_{max}$(film)/$cm^{-1}$ 2920s, 2774m, 1604m and 1495m. The product was used immediately in coupling reactions.

4-(tert-*Butyldiphenylsiloxymethyl*)*aniline* **18**.—The reaction was carried out as above for the keto analogue **6**, with 4-hydroxymethylaniline (1.0 g, 8.14 mmol), imidazole (1.38 g, 20.3 mmol), and *tert*-butylchlorodiphenylsilane (2.50 $cm^3$, 9.77 mmol) in dry DMF (10 $cm^3$). The reaction mixture was worked up as before and the product purified by flash chromatography (ethyl acetate–petroleum, 1:5) to yield the *aniline* **18** (2.79 g, 95%) as a colourless oil; $\nu_{max}$(film)/$cm^{-1}$ 3500s, 3375s, 2857s, 1735s, 1624s, 1519s, 1472s and 1428s; $\delta_H$(270 MHz; $CDCl_3$) 1.19 (9 H, s, $Bu^t$), 4.77 (2 H, s, $CH_2$), 6.71 (2 H, d, *J* 8.1, 2,6-H), 7.22 (2 H, d, *J* 8.1, 3,5-H), 7.47 (6 H, m, Ar) and 7.81 (4 H, m, Ar); $\delta_C$(125 MHz; $CDCl_3$) 19.23 ($CMe_3$), 26.83 ($CMe_3$), 65.52 ($CH_2$), 114.85 (C-2), 127.51 (C-3), 127.57 (C-3′), 129.54 (C-4′), 131.01 (C-1), 133.77 (C-1′), 135.53 (C-2′) and 145.29 (C-4); *m*/*z* (FAB) 361 ($M^+$, 5%), 360 ($M^+$ − H, 13), 304 ($M^+ - Bu^t$, 38), ($M^+ + H - OTBDPS$, 100), 199 ($HOSiPh_2^+$, 24), 135 ($C_8H_7O_2^+$, 24) and ($M^+$ − OTBDPS, 100) (Found: $M^+$, 361.1851. $C_{23}H_{27}NOSi$ requires *M*, 361.1861).

4-(tert-*Butyldiphenylsiloxymethyl*)*phenyl Isocyanate* **19**.—Triphosgene (154 mg, 0.52 mmol) was added to a solution of the aniline **18** (470 mg, 1.30 mmol) in toluene (10 $cm^3$) and the mixture was heated at 80 °C for 2 h. The solvent was removed under reduced pressure and the product was purified by flash chromatography (diethyl ether–hexane, 1:5) to yield the isocyanate **19** (250 mg, 50%) as an oil; $\nu_{max}$(film)/$cm^{-1}$ 2931s, 2273s, 1642m, 1604m and 1514m; $\delta_H$(270 MHz; $CDCl_3$) 1.09 (9 H, s, $Bu^t$), 4.75 (2 H, s, $CH_2$), 7.07 (2 H, d, *J* 8.1, 2,6-H), 7.40 (8 H, m, Ar) and 7.72 (4 H, m, Ar).

2-*Bromo*-4-(tert-*butyldiphenylsiloxymethyl*)*aniline* **20**.—*N*-Bromosuccinimide (50 mg, 0.277 mmol) was added to a solution of the aniline **18** (100 mg, 0.277 mmol) in chloroform (10 $cm^3$) and the reaction mixture was stirred for 3 h. Water was added (20 $cm^3$) and the product was extracted into dichloromethane (3 × 20 $cm^3$). The combined organic extracts were dried, evaporated and purified by flash chromatography

(ethyl acetate–hexane, 1 : 10) to yield firstly a small quantity of the dibrominated material (10 mg, 7%; *m/z* 517) which was not further characterised. This was followed by the *brominated aniline* **20** (70 mg, 57%) as a colourless oil; $\nu_{max}$(film)/cm$^{-1}$ 3476s, 3382s, 2930s, 1620s and 1540s; $\delta_H$(270 MHz; $CDCl_3$) 1.11 (9 H, s, Bu$^t$), 4.64 (2 H, s, $CH_2$), 6.73 (1 H, d, *J* 8.3, 6-H), 7.07 (1 H, dd, *J* 8.3 and 2.0, 5-H), 7.40 (7 H, m, Ar) and 7.72 (4 H, m, Ar); *m/z* (FAB) 440 ($M^+$ + H, 25%), 384 ($M^+$ − Bu$^t$, 87), 186 ($M^+$ − OTBDPS, 100) and 135 ($C_8H_7O_2^+$, 93) (Found: $M^+$, 439.0991. $C_{23}H_{26}BrNOSi$ requires *M*, 439.0967).

Finally, unchanged starting material (20 mg, 20%) was eluted.

3-(tert-*Butyldiphenylsiloxymethyl*)*aniline* **21**.—The reaction was carried out as above for the keto-analogue **7**, with 3-hydroxymethylaniline (1.0 g, 8.14 mmol), imidazole (1.39 g, 20.4 mmol), and *tert*-butylchlorodiphenylsilane (2.10 cm$^3$, 8.14 mmol) in dry DMF (10 cm$^3$). The reaction mixture was worked up as before and purified by flash chromatography (ethyl acetate–petroleum, 1 : 5) to yield the *silylated aniline* **21** (2.53 g, 86%), as a colourless oil, $R_f$ 0.38 (diethyl ether–hexane, 1 : 1); $\nu_{max}$(film)/cm$^{-1}$ 3450s, 3376s, 2930s, 1736s, 1620s, 1592s, 1463s and 1427s; $\delta_H$(270 MHz; $CDCl_3$) 1.10 (9 H, s, Bu$^t$), 3.65 (2 H, br, $NH_2$), 4.70 (2 H, s, $CH_2$), 6.57 (1 H, dd, *J* 8.1 and 1.0 Hz, 6-H), 6.73 (1 H, d, *J* 1.0, 2-H), 6.74 (1 H, d, *J* 8.1, 4-H), 7.12 (1 H, t, *J* 8.1, 5-H), 7.40 (6 H, m, Ar) and 7.65 (4 H, m, Ar); $\delta_C$(125 MHz; $CDCl_3$) 19.31 (*C*Me$_3$), 26.86 (C*Me*$_3$), 65.43 ($CH_2$), 112.67 (C-2), 113.64 (C-6), 116.22 (C-4), 127.67 (C-3′), 129.05 (C-5), 129.62 (C-4′), 133.60 (C-1′), 135.57 (C-2′), 142.38 (C-3) and 146.34 (C-1); *m/z* (FAB) 362 ($M^+$ + H, 17%), 304 ($M^+$ − Bu$^t$, 87), 284 ($M^+$ − Ph, 13), 226 ($M^+$ − $C_6H_6$ − Bu$^t$, 20), 199 ($HOSiPh_2^+$, 14), 135 ($C_8H_7O_2^+$, 35) and ($M^+$ − OTBDPS, 100) (Found: $M^+$ + 1, 362.1931. $C_{23}H_{28}NOSi$ requires *M*, 362.1940).

3-(tert-*Butyldiphenylsiloxymethyl*)*phenyl Isocyanate* **22**.—The reaction was carried out as above for the *para*-isomer **19** with triphosgene (211 mg, 0.706 mmol) and the aniline **21** (640 mg, 1.77 mmol) in toluene (25 cm$^3$). The reaction mixture was worked up as before and purified by flash chromatography (diethyl ether–hexane, 1 : 10) to yield the isocyanate **22** (600 mg, 88%) as a colourless oil, $R_f$ (0.72; diethyl ether–hexane, 1 : 1); $\nu_{max}$(film)/cm$^{-1}$ 2932s, 2268s, 1610m, 1590m and 1471m; $\delta_H$(270 MHz; $CDCl_3$) 1.09 (9 H, s, Bu$^t$), 4.72 (2 H, s, $CH_2$), 6.96 (1 H, d, *J* 7.7, 6-H), 7.05 (1 H, s, 2-H), 7.14 (1 H, d, *J* 7.9, 4-H), 7.26 (1 H, dd, *J* 7.9 and 7.7, 5-H), 7.40 (8 H, m, Ar) and 7.67 (4 H, m, Ar); $\delta_C$(125 MHz; $CDCl_3$) 19.30 (*C*Me$_3$), 26.85 (C*Me*$_3$), 64.93 ($CH_2$), 122.30 (C-2), 123.14 (C-6), 123.33 (C-4), 124.78 (NCO), 127.78 (C-3′), 129.32 (C-5), 129.81 (C-4′), 133.28 (C-1′), 133.42 (C-1), 135.56 (C-2′) and 142.96 (C-3); *m/z* (FAB) 386 ($M^+$ − H, 3%), 330 ($M^+$ − Bu$^t$, 87), 252 ($M^+$ − $C_6H_6$ − Bu$^t$, 19), 199 ($HOSiPh_2^+$, 25) and 135 ($C_8H_7O_2^+$, 45).

4-*Bromo*-3-(tert-*butyldiphenylsiloxymethyl*)*aniline* **23**.—The reaction was carried out as above for the *para*-isomer with *N*-bromosuccinimide (79 mg, 0.443 mmol) and the aniline **21** (160 mg, 0.443 mmol) in chloroform (15 cm$^3$). The reaction mixture was worked up as before and purified by flash chromatography (ethyl acetate–hexane, 1 : 10) to yield the *brominated aniline* **23** (47 mg, 24%) as a colourless oil; $\nu_{max}$(film)/cm$^{-1}$ 3460s, 3400s, 2930s, 1610s and 1520s; $\delta_H$(270 MHz; $CDCl_3$) 1.15 (9 H, s, Bu$^t$), 4.76 (2 H, s, $CH_2$), 6.72 (1 H, dd, *J* 8.3 and 3.0, 6-H), 7.14 (1 H, d, *J* 3.0, 2-H), 7.30 (1 H, d, *J* 8.3, 5-H), 7.48 (6 H, m, Ar) and 7.78 (4 H, m, Ar); *m/z* (FAB) 440 ($M^+$ − H, 10%), 384 ($M^+$ − Bu$^t$, 83), 364 ($M^+$ − Ph, 12), 304 ($M^+$ − HBr − Bu$^t$, 66) and 135 ($C_8H_7O_2^+$, 100).

Further elution gave traces of dibrominated material.

2-(2′-tert-*Butyldiphenylsiloxyethoxy*)*ethylamine* **24**.—Imidazole (655 g, 9.62 mmol) and then *tert*-butylchlorodiphenylsilane (1.0 cm$^3$, 3.85 mmol) were added to 2-(2-aminoethoxy)ethanol. The reaction mixture was stirred for 18 h and then dichloromethane (20 cm$^3$) and water (20 cm$^3$) were added and the product was extracted into dichloromethane (3 × 30 cm$^3$). The combined organic extracts were washed with brine (30 cm$^3$), dried and evaporated to yield the pure *silyl ether* **24** (1.29 g, 98%) as a colourless oil; $\nu_{max}$(film)/cm$^{-1}$ 3400br, 2930s and 1600m; $\delta_H$(270 MHz; $CDCl_3$) 1.05 (9 H, s, Bu$^t$), 2.05 (2 H, br, $NH_2$), 2.83 (2 H, t, *J* 5.2, 1-H), 3.50 (2 H, t, *J* 5.2 Hz, 2-H), 3.57 (2 H, t, *J* 5.2, 1′-H), 3.81 (2 H, t, *J* 5.2, 2′-H), 7.40 (6 H, m, Ar) and 7.70 (4 H, m, Ar); $\delta_C$(125 MHz; $CDCl_3$) 19.17 (*C*Me$_3$), 26.79 (C*Me*$_3$), 41.81 (C-1), 63.43 (C-2), 72.20 (C-1′), 73.21 (C-2′), 127.60 (C-3″), 129.59 (C-4″), 133.70 (C-1″) and 135.57 (C-2″); *m/z* (FAB) 344 ($M^+$ + H, 100%), 199 ($HOSiPh_2^+$, 15) and 135 ($C_8H_7O_2^+$, 25) (Found: $M^+$ + 1, 344.2070. $C_{20}H_{30}NO_2Si$ requires *M*, 344.2046).

2-(2-tert-*Butyldiphenylsiloxyethoxy*)*ethyl Isocyanate* **25**.—Triphosgene (303 mg, 0.973 mmol), was added to a solution of DMAP (711 mg, 5.84 mmol) in dry dichloromethane (50 cm$^3$). The temperature of the solution was raised to 50 °C and to this was added, dropwise over 2 h, a solution of the siloxy amine **24** also in dichloromethane (30 cm$^3$). The reaction mixture was cooled to room temperature and stirred for a further 18 h. The solvent was removed under reduced pressure and the product was purified by flash chromatograhy (diethyl ether–hexane, 1 : 10) to give the *isocyanate* **25** (516 mg, 48%) as a colourless oil; $\nu_{max}$(film)/cm$^{-1}$ 2930s, 2224s and 1428m; $\delta_H$(270 MHz; $CDCl_3$) 1.11 (9 H, s, Bu$^t$), 3.39 (2 H, t, *J* 5.2, 1-H), 3.65 (4 H, m, 2-H and 1′-H), 3.88 (2 H, t, *J* 5.2, 2′-H), 7.40 (6 H, m, Ar) and 7.70 (4 H, m, Ar); $\delta_C$(125 MHz; $CDCl_3$) 19.17 (*C*Me$_3$), 26.79 (C*Me*$_3$), 41.81 (C-1), 63.43 (C-2), 72.20 (C-1′), 73.21 (C-2′), 127.60 (C-3″), 129.59 (C-4″), 133.70 (C-1″) and 135.57 (C-2″); *m/z* (FAB) 344 ($M^+$ − H, 100%), 199 ($HOSiPh_2^+$, 15) and 135 ($C_8H_7O_2^+$, 25).

## Acknowledgements

We thank Mr. H. Desai of the MOD for helpful discussions, the SERC Innovative Polymer Synthesis Initiative and the MOD for funding this programme and the SERC Mass Spectrometry Service Centre, Swansea for the mass spectral data.

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*Paper* 4/06483F
*Received* 24*th October* 1994
*Accepted* 10*th November* 1994