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SYNTHESIS OF SOME CARBON-FUNCTIONAL ORGANOSILICON COMPOUNDS

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Summary

The synthesis are reported of the carbon-functional organosilicon compounds $X(CH_2)_3Si(OEt)Me_2$ and p-$XC_6H_4Si(OEt)Me_2$ having X = —OH, —NH_2, and —CO_2H.

Introduction

Carbon-functional silanes bearing functional groups such as amine etc. are of interest because of their potential importance as precursors in the dental and textile industries [1]. Bearing this in mind, we have prepared some organosilanes bearing carbon-functional groups such as —OH, —NH_2, or —CO_2H. The presence of an alkoxy group on the silicon atom also makes it possible to link these organosilanes to other organometallic compounds, such as organotitanium compounds via Si—O—M bonds.

Results and discussion

The following six model compounds were selected for synthesis: (i) $Me_2(EtO)Si(CH_2)_3X$ and (ii) p-$Me_2(EtO)SiC_6H_4X$ where X = —OH, —NH_2, and —CO_2H.

The two most common methods [viz. hydrosilylation and Grignard or organolithium methods] were used for forming Si—C bonds. The first one was selected for the aliphatic series and the second for the aryl series.

Neither of these reactions could be applied directly to the synthesis envisaged here because: (a) the Si—H bond reacts with alcohols, amines and carboxylic acids [2], and (b) Grignard or organolithium reagents react with acidic hydrogen and also with the unsaturated groups such as those present in the carboxyl groups [3]. Consequently it was necessary to protect the functional groups.

The acidic hydrogen position can conveniently be protected by the trimethylsilyl groups in both types of reactions [4], and this technique was used for both

the aliphatic and aromatic compounds:

$$ROH + Me_3SiCl \xrightarrow[C_6H_6]{Et_3N} ROSiMe_3$$

$$RNH_2 + EtMgBr \xrightarrow[THF]{Me_3SiCl} RN(SiMe_3)_2$$

$$RNH_2 + (Me_3Si)_2NH \rightarrow RN(SiMe_3)_2$$

$$RCO_2H + Me_3SiCl \xrightarrow[C_6H_6]{Et_3N} RCO_2SiMe_3$$

where R = alkyl, aryl.

For hydrosylilation of the allyl series, dimethyl(ethoxy)silane, $Me_2(EtO)SiH$ [5], was used directly.

The key steps in the synthesis are summarized in Schemes 1 and 2.

The aliphatic compounds were synthesized by protective silylation (IIa—IIc), hydrosilylation with $Me_2(EtO)SiH$ (IIIa—IIIc), and finally solvolytic removal of the protective groups, to give the final compounds (IVa—IVc) in good yields.

For the aromatic compounds, the functional groups were protected as for the aliphatic compounds (VIa—VIc): silylation was carried out with dichlorodimethylsilane, Me_2SiCl_2 (VIIa—VIIb) and (dimethylamino)dimethylchlorosilane. $Me_2(Me_2N)SiCl$ (VIIIa—VIIIc). The solvolytic removal of the functional groups from the chlorosilanes (VIIa—VIIb) poses a problem as this would generate HCl, which is known to cleave the aryl—silicon bond [6]. To avoid this, the chlorosilanes were converted into aminosilanes with anhydrous dimethylamine, Me_2NH (VIIIa—VIIIb). We also used (dimethylamino)dimethylchlorosilane to silylate the Grignard and organolithium reagents. The aminosilane route was preferred because of the facile and mild reaction conditions needed for the solvolysis. The amine generated during solvolysis did not cleave the aryl—silicon or the alkyl—silicon bonds, and good yields of the final products (IXa—IXc) were obtained:

$$Me_2(Me_2N)SiC_6H_4X \xrightarrow{EtOH} Me_2(EtO)SiC_6H_4Y + Me_2NH$$

where X = —$OSiMe_3$, —$N(SiMe_3)_2$, —CO_2Li
and Y = —OH, —NH_2, —CO_2H.

SCHEME 1

$$CH_2{=}CHCH_2OH \xrightarrow{(i)} CH_2{=}CHCH_2OSiMe_3 \xrightarrow{(iii)} Me_2(EtO)Si(CH_2)_3OSiMe_3 \xrightarrow{(iv)} Me_2(EtO)Si(CH_2)_3OH$$

(Ia) (IIa) (IIIa) (IVa)

$$CH_2{=}CHCH_2NH_2 \xrightarrow{(ii)} CH_2{=}CHCH_2N(SiMe_3)_2 \xrightarrow{(iii)} Me_2(EtO)Si(CH_2)_3N(SiMe)_2 \xrightarrow{(iv)} Me_2(EtO)Si(CH_2)_3NH_2$$

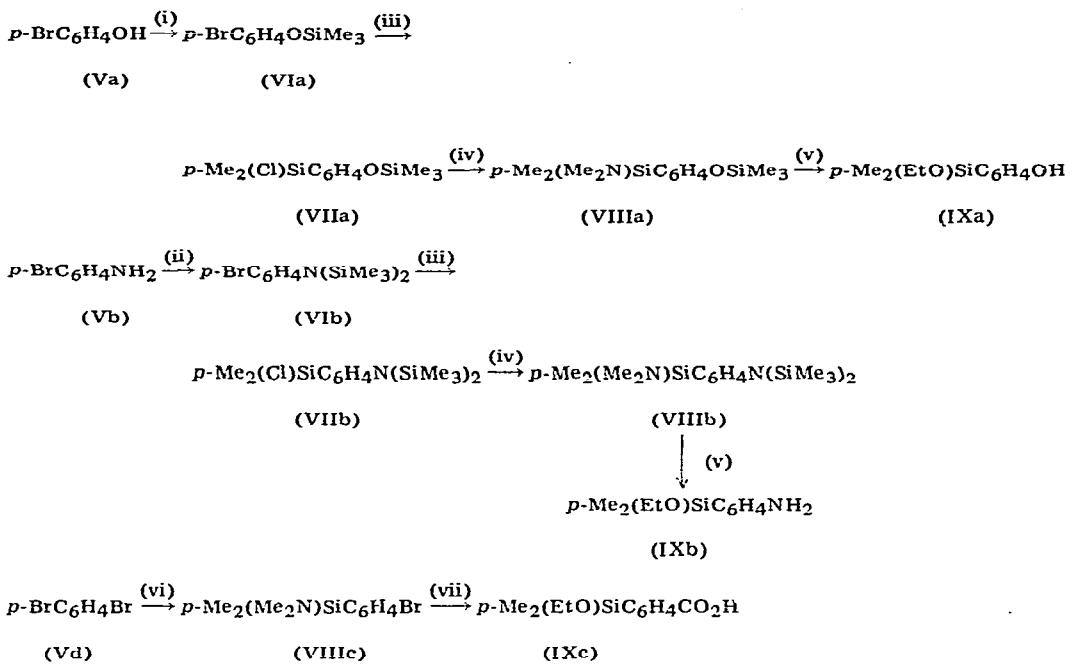
(Ib) (IIb) (IIIb) (IVb)

$$CH_2{=}CHCH_2CO_2H \xrightarrow{(i)} CH_2{=}CHCH_2CO_2SiMe_3 \xrightarrow{(iii)} Me_2(EtO)Si(CH_2)_3CO_2SiMe_3 \xrightarrow{(iv)} Me_2(EtO)Si(CH_2)_3CO_2H$$

(Ic) (IIc) (IIIc) (IVc)

(i) Me_3SiCl/NEt_3; (ii) $(Me_3Si)_2NH$; (iii) $Me_2(EtO)SiH/H_2PtCl_6 \cdot 6\ H_2O$; (iv) EtOH.

SCHEME 2



(i) Me_3SiCl/pyridine; (ii) n-BuLi/Me_3SiCl; (iii) n-BuLi/Me_2SiCl_2; (iv) Me_2NH/Et_2O; (v) EtOH; (vi) Mg/$Me_2(Me_2N)SiCl$; (vii) n-BuLi/CO_2/EtOH.

Lithiation of p-$BrC_6H_4CO_2SiMe_3$ (VIc), and subsequent coupling with Me_2SiCl_2, did not give the product (IXc). As an alternative route, we converted p-dibromobenzene into the monosilylated product $Me_2(Me_2N)SiC_6H_4Br$ (VIIIc). The product was then successfully converted into the corresponding benzoic acid, $Me_2(EtO)SiC_6H_4CO_2H$-p (IXc), in good yield by using n-butyllithium and carbon dioxide followed by ethanolysis.

Experimental

The distillations were carried out with precision made Vigreux columns equivalent to ca. 12 theoretical plates. Moisture sensitive compounds (notably chlorosilanes, aminosilanes, Grignard reagents and organolithium compounds) were manipulated under dry nitrogen.

NMR spectra were recorded on a Varian A60 or T60 instrument, with tetramethylsilane as internal standard. The results are given as values in ppm. The IR spectra were recorded on a Perkin-Elmer 237 spectrophotometer, by using films for liquids and Nujol mulls for solids.

The reported molecular weights refer to the parent ion peak as recorded on an AE1 MS9 spectrometer.

(A) Preparation of O-, and N-silylated compounds

(i) Allyloxy(trimethyl)silane, ($Me_3SiOCH_2CH{=}CH_2$) (IIa). Chlorotrimethylsilane (174 g, 1.6 mol), allyl alcohol (Ia) (87 g, 1.5 mol) and triethylamine (162 g, 1.6 mol) gave the product in 60% yield, b.p. 101°C, n_D^{25} 1.3949 (lit. [7], b.p. 100—100.2°C, n_D^{30} 1.3904). IR (liquid film), ν(C=C), 1605m; ν(Si—Me), 1250s, 820s; ν(Si—O—C), 1070 cm^{-1}. NMR (neat), Me_3Si δ —0.20(s); CH_2 3.80(m), 4.80(m); CH 5.30(m) ppm.

(ii) N,N-Bistrimethylsilylallylamine, ($CH_2{=}CHCH_2N(SiMe_3)_2$] (IIb). Allylamine (Ib) (46.6 g, 0.8 mol), hexamethyldisilazane (106 g, 0.88 mol) and ammonium sulphate (2 g) gave the product (50%), b.p. 102°C/55 mmHg, n_D^{25} 1.4357 (lit. [8], b.p. 179°C/741 mmHg, n_D^{25} 1.4367), IR (liquid film), ν(C=C), 1650m; ν(Me—Si), 1255s(sh), 845s cm^{-1}. NMR (CCl_4), Me_3Si δ 0.00(s); CH_2 3.38(m), 4.95(m); CH 5.66(m) ppm.

(iii) O-Trimethylsilylvinylacetate, ($CH_2{=}CHCH_2CO_2SiMe_3$) (IIc). Vinyl acetic acid (Ic) (100 g, 1.2 mol), triethylamine (121.5 g, 1.2 mol) and chlorotrimethylsilane (130.2 g, 1.2 mol) gave the compound (80%), b.p. 69°C/40 mmHg, n_D^{27} 1.4128. (Found: C, 53.0; H, 8.8%; mol. wt. 158. $C_7H_{14}O_2Si$ calcd.: C, 53.1; H, 8.9%; mol. wt. 158). IR (liquid film), ν(C=O), 1730s; ν(C=C), 1650m; ν(Me—Si), 1260s(sh), 855s; ν(Si—O—C), 1100s cm^{-1}. NMR (CCl_4), Me_3Si δ 0.15(s); CH_2 2.90(m), 5.09(m); CH 5.83(m) ppm.

(iv) (p-Bromophenoxy)trimethylsilane, (p-$BrC_6H_4OSiMe_3$) (VIa). p-Bromophenol (Va) (173 g, 1 mol), dry pyridine (79 g, 1 mol) and chlorotrimethylsilane (108.5 g, 1 mol) gave the product (90%), b.p. 80°C/0.5 mmHg, n_D^{20} 1.5235 (lit. [9], b.p. 98°C/7 mmHg, n_D^{20} 1.5145). (Found: C, 43.7; H, 5.0%; mol. wt. 245. $C_9H_{13}BrOSi$ calcd.: C, 44.0; H, 5.3%; mol. wt. 245). IR (liquid film), ν(aromatic C—H), 1585s; ν(Me—Si), 1250s(sh), 835s; ν(p-subst.), 820s cm^{-1}. NMR (CCl_4), Me_3Si δ 0.15(s); Ph 7.00(m) ppm.

(v) p-Bromo-N,N-bistrimethylsilylaniline, (p-$BrC_6H_4N(SiMe_3)_2$] (VIb). Lithiation of p-bromoaniline (Vb) (86 g, 0.5 mol) at low temperature with n-butyllithium and subsequent coupling with chlorotrimethylsilane (108.5 g, 1 mol) gave the compound (90%), b.p. 80°C/0.2 mmHg, n_D^{25} 1.5178 (lit. [10], b.p. 106°C/1.2 mmHg, n_D^{25} 1.5140). IR (liquid film), ν(aromatic C—H), 1600s(sh); ν(Me—Si), 1255s(sh), 840s; ν(p-subst.), 815s cm^{-1}. NMR (CCl_4), Me_3Si δ —0.06(s); Ph 7.00(m) ppm.

(vi) p-Bromo-O-trimethylsilylbenzoate, (p-$BrC_6H_4CO_2SiMe_3$) (VIc). p-Bromobenzoic acid (Vc) 201 g, 1 mol), chlorotrimethylsilane (108.5 g, 1 mol) and triethylamine (121 g, 1.2 mol) gave the product (70%), b.p. 78—82°C/0.5 mmHg, n_D^{25} 1.5185. (Found: C, 44.1; H, 5.1%; mol. wt. 273. $C_{10}H_{13}Br_2Osi$ calcd.: C, 44.0; H, 4.8%; mol. wt. 273). IR (liquid film), ν(C=O), 1700s; ν(aromatic C—H), 1590s; ν(Me—Si), 1250s, 840s; ν(p-subst.), 820s cm^{-1}. NMR (CCl_4), Me_3Si δ 0.20(s); Ph 7.35(m) ppm.

(B) Hydrosilylations

(i) 3-Dimethyl(ethoxy)silyl-O-trimethylsilylpropanol, [$Me_2(OEt)Si(CH_2)_3$-$OSiMe_3$] (IIIa). To a mixture of allyloxy(trimethyl)silane (IIa) (13 g, 0.1 mol) and chloroplatinic acid (0.3 cm^3 of 0.1 *M* solution in isopropanol), maintained at 60°C, dimethyl(ethoxy)silane (12.5 g, 0.12 mol) was added slowly. The reaction mixture was boiled under reflux for 4 h. The fractionation of the reac-

tion mixture afforded the product (70%), b.p. 46°C/0.6 mmHg, n_D^{24} 1.4120. (Found: C, 51.1; H, 11.0%; mol. wt. 243. $C_{10}H_{26}O_2Si_2$ calcd.: C, 51.3; H, 11.1%; mol. wt. 243). IR (liquid film), ν(Me—Si), 1255s, 840s; ν(Si—O—C), 1100s(br) cm^{-1}. NMR (neat), Me_3Si and Me_2Si δ —0.16(d); CH_3 0.90(t); CH_2O 3.33(m); CH_2 0.30(m), 1.30(m) ppm.

(ii) 3-Dimethyl(ethoxy)silyl-N,N-bistrimethylsilylpropylamine, [$Me_2(EtO)Si(CH_2)_3N(SiMe_3)_2$] (IIIb). The reaction, under similar conditions to B(i), with *N,N*-bistrimethylsilylpropylamine (IIb) and dimethyl(ethoxy)silane gave the compound in 77% yield, b.p. 70°C/0.15 mmHg, n_D^{26} 1.4346. (Found: C, 51.5; H, 11.7; N, 4.7%; mol. wt. 305. $C_{13}H_{35}NOSi_3$ calcd.: C, 51.1; H, 11.4; N, 4.6%; mol. wt. 305). IR (liquid film), ν(Me—Si), 1250s(sh), 835s; ν(Si—O—C), 1110s, 1070s cm^{-1}. NMR (CCl_4), Me_3Si and Me_2Si δ 0.00(d); CH_3 1.05(t); CH_2O 3.50(q); CH_2 0.30(m), 1.23(m), 2.63(m) ppm.

(iii) 3-Dimethyl(ethoxy)silyl-O-trimethylsilylbutyrate, [$Me_2(EtO)Si(CH_2)_3CO_2SiMe_3$] (IIIc). *O*-Trimethylsilylvinylacetate (IIc) and dimethyl(ethoxy)-silane reacted as in B(i) and the fractionation of the reaction mixture gave the desired product (80%), b.p. 52°C/0.08 mmHg, n_D^{20} 1.4266. (Found: C, 50.2; H, 9.9%; mol. wt. 262. $C_{11}H_{26}O_3Si_2$ calcd.: C, 50.4; H, 9.9%; mol. wt. 262). IR (liquid film), ν(C=O), 1725s; ν(Me—Si), 1255s(sh), 845s; ν(Si—O—C), 1110s, 1080s cm^{-1}. NMR (CCl_4), Me_2Si δ 0.13(s); Me_3Si 0.32(s); CH_3 1.20(t); CH_2O 3.68(q); CH_2 0.63(m), 1.66(m), 2.33(t) ppm.

(C) Grignard and organolithium syntheses

(i) [p-Chloro(dimethyl)silyl]phenoxytrimethylsilane, [p-$Me_2(Cl)SiC_6H_4OSiMe_3$] (VIIa). n-Butyllithium (0.3 mol of 1.6 *M* solution in hexane) was added slowly to a stirred solution of (*p*-bromophenoxy)trimethylsilane (VIa) (61.3 g, 0.25 mol) in diethyl ether (200 cm^3) maintained at —40° C. After the addition, the reaction mixture was allowed to warm to room temperature and finally boiled under reflux for 0.5 h. The reaction mixture was cooled again to —40°C and was added to dichlorodimethylsilane (32 g, 0.25 mol), kept stirred at —60°C in diethyl ether (200 cm^3). The reaction mixture was heated and subsequently boiled under reflux for 3 h. Precipitated salts were filtered off and the fractionation of the filtrate gave the desired product (40%), b.p. 80°C/0.05 mmHg, n_D^{25} 1.5092. (Found: C, 51.0; H, 7.1; Cl, 13.7%; mol. wt. 258. $C_{11}H_{19}ClOSi_2$ calcd.: C, 51.0; H, 7.3; Cl, 13.8%; mol. wt. 258.5). IR (liquid film), ν(aromatic C—H), 1585s; ν(Me—Si), 1255s, 820s; ν(*p*-subst.), 805s cm^{-1}. NMR (CCl_4), Me_2Si δ —0.15(s); Me_3Si 0.45(s); Ph 7.00(m) ppm, and bis(*p*-phenoxytrimethylsilyl)dimethylsilane (24%), b.p. 130°C/0.01 mmHg, n_D^{25} 1.5500. (Found: C, 61.8; H, 8.1%; mol. wt. 388. $C_{20}H_{32}O_3Si_3$ calcd.: C, 61.9; H, 8.2%; mol. wt. 388. IR (liquid film), ν(aromatic C—H), 1590s; ν(Me—Si), 1250s, 820s; ν(*p*-subst.), 805s cm^{-1}. NMR (CCl_4), Me_2Si δ —0.28(s); Me_3Si 0.60(s); Ph 7.00(m) ppm.

(ii) p-[N,N-Bis(trimethylsilyl)aminophenyl]chlorodimethylsilane, [p-$Me_2(Cl)SiC_6H_4N(SiMe_3)_2$] (VIIb). The lithiation of *p*-bromo-*N,N*-bis(trimethylsilyl)aniline (VIb) and its coupling with dichlorodimethylsilane, described in C(i) above, gave the desired product (82%), b.p. 70—74°C/0.01 mmHg, n_D^{26} 1.4950. (Found: C, 50.9; H, 8.4; Cl, 10.9; N, 4.2%; mol. wt. 329. $C_{14}H_{28}ClNSi_3$ calcd.: C, 51.0; H, 8.5; Cl, 10.8; N, 4.2%; mol. wt. 329.5). IR (liquid film), ν(aromatic C—H), 1600s; ν(Me—Si), 1260s, 830s; ν(*p*-subst.), 805s cm^{-1}. NMR (CCl_4), Me_2Si δ

—0.75(s); Me_3Si 0.20(s); Ph 7.35(m) ppm, and bis[*p*-(*N*,*N*-bistrimethylsilylamino)-phenyl]dimethylsilane (4%), b.p. 110°C/0.01 mmHg, n_D^{26} 1.4968. Found: C, 58.8; H, 9.2; N, 5.3%; mol. wt. 530. $C_{26}H_{50}N_2Si_5$ calcd.: C, 58.9; H, 9.4; N, 5.3%; mol. wt. 530. IR (liquid film), ν(aromatic C—H), 1592s(sh); ν(Me—Si), 1260s, 830s; ν(*p*-subst.), 805s cm^{-1}. NMR (CCl_4), Me_2Si δ —0.80(s); Me_3Si 0.30(s); Ph 7.25(m) ppm.

(D) Conversion of chloro- into dimethylaminosilanes

(i) [p-Dimethyl(dimethylamino)silyl]phenoxytrimethylsilane, [p-$Me_2(Me_2N)$-$SiC_6H_4OSiMe_3$] (VIIIa). [*p*-Chloro(dimethyl)silyl]phenoxytrimethylsilane (VIIa) and anhydrous dimethylamine in diethyl ether gave the product (84%), b.p. 100°C/0.05 mmHg, n_D^{25} 1.4995. (Found: C, 58.3; H, 9.1; N, 5.3%; mol. wt. 267. $C_{13}H_{25}NOSi_2$ calcd.: C, 58.4; H, 9.3; N, 5.2%; mol. wt. 267). IR (liquid film), ν(aromatic C—H), 1600s; ν(Me—Si), 1270s, 838s; ν(*p*-subst.), 805s cm^{-1}. NMR (CCl_4), Me_3Si δ 0.10(s); Me_2Si 0.12(s); Me_2N 2.40(s); Ph 6.85(m) ppm. The same compound was prepared in 70% yield by treating an ethereal solution of (*p*-lithiophenoxy)trimethylsilane with chloro(dimethylamino)dimethylsilane [5], in diethyl ether, and then by the usual working up.

(ii) p-[N,N-Bis(trimethylsilyl)aminophenyl]dimethyl(dimethylamino)silane [p-$Me_2(Me_2N)SiC_6H_4N(SiMe_3)_2$] (VIIIb). Anhydrous dimethylamine and [*p*-*N*,*N*-bis(trimethylsilyl)aminophenyl]chlorodimethylsilane (VIIb) gave the compound (75%), b.p. 100°C/0.01 mmHg, n_D^{18} 1.4880. (Found: C, 56.8; H, 10.1; N, 8.1%; mol. wt. 338. $C_{16}H_{34}N_2Si_3$ calcd.: C, 56.8; H, 10.1; N, 8.3%; mol. wt. 338). IR (liquid film), ν(aromatic C—H), 1605s; ν(Me—Si), 1265s(sh), 845(s); ν(*p*-subst.), 820s cm^{-1}. NMR (CCl_4), Me_3Si δ 0.05(s); Me_2Si 0.15(s); Me_2N 2.30(s); Ph 7.00(m) ppm. The same compound was prepared in 81% yield by treating an ethereal solution of *p*-lithio-*N*,*N*-bis(trimethylsilyl)aniline with chloro(dimethylamino)dimethylsilane in diethyl ether.

(E) Organolithium syntheses

(i) p-Bromophenyl(dimethylamino)dimethylsilane. [p-$BrC_6H_4Si(NMe_2)Me_2$] (VIIIc). Chloro(dimethylamino)dimethylsilane (68 g, 0.5 mol) in diethyl ether (100 cm^3) was added to *p*-bromophenylmagnesium bromide (0.5 mol), prepared from *p*-dibromobenzene (Vd) and magnesium turnings at —10°C in ether. After the addition, the reaction mixture was allowed to warm and was subsequently boiled under reflux for 4 h. The precipitated salts were filtered off and the filtrate was fractionated to give the product (75%), b.p. 80°C/0.01 mmHg, n_D^{22} 1.5289. (Found: C, 46.4; H, 6.2; N, 5.4%; mol. wt. 258). $C_{10}H_{16}BrNSi$ calcd.: C, 46.5; H, 6.2; N, 5.4%; mol. wt. 258). IR (liquid film), ν(aromatic C—H); 1590s; ν(Me—Si), 1250s, 818s; ν(*p*-subst.), 800s cm^{-1}. NMR (CCl_4), Me_2Si δ 0.30(s); Me_2N 2.50(s); Ph 7.40(m) ppm.

(ii) p-Dimethyl(ethoxy)silylbenzoic acid, [p-$Me_2(EtO)SiC_6H_4CO_2H$] (IXc). n-Butyllithium (0.12 mol of 1.6 *M* solution in hexane) was added to *p*-bromophenyl(dimethylamino)dimethylsilane (VIIIc) (25.8 g, 0.1 mol) in diethyl ether (100 cm^3) at 0°C. The reaction mixture was allowed to warm and subsequently boiled under reflux for 0.5 h. The reaction mixture was cooled to —10°C and was slowly added to a saturated solution of carbon dioxide in diethyl ether (100 cm^3) maintained at —40°C, whilst a fast stream of CO_2 was bubbled through

the mixture for 1 h. The yellow reaction mixture was allowed to warm to room temperature and absolute ethanol (25 cm^3) was added. The mixture separated into two layers after standing overnight. The upper ethereal layer was separated and the volatile products were removed under vacuum. The residual oil was triturated with petroleum ether (40—60°C) and stored in a freezer. White crystalline products were isolated (75%), m.p. 95—96°C ($CHCl_3$—pet. ether). (Found: C, 58.8; H, 7.1%; mol. wt. 224. $C_{11}H_{16}O_3Si$ calcd.: C, 58.9; H, 7.1%; mol. wt. 224). IR (nujol), ν(aromatic C—H), 1600s; ν(C=O), 1720s; ν(Me—Si), 1260s(sh), 820s; ν(*p*-subst.), 810s cm^{-1}. NMR ($CDCl_3$-DMSO), Me_2Si δ 0.10(s); CH_3 1.30(t); CH_2O 1.83(m); Ph 7.38(m); OH 12.9(s,br) ppm.

(F) Ethanolysis of O- and N-trimethylsilyl derivatives

(i) 3-Dimethyl(ethoxy)silylpropan-1-ol, [$Me_2(EtO)Si(CH_2)_3OH$] (IVa). 3-Dimethyl(ethoxy)silyl-*O*-trimethylsilylpropanol (IIIa) and excess absolute ethanol were refluxed for 1 h. The mixture was fractionated to give the product (90%), b.p. 66°C/10 mmHg, n_D^{18} 1.4468. (Found: C, 51.6; H, 11.0%; mol. wt. 162. $C_7H_{18}O_2Si$ calcd.: C, 51.8; H, 11.1%; mol. wt. 162). IR (liquid film), ν(OH), 3420s(br); ν(Me—Si), 1262s(sh), 850s; ν(Si—O—C), 1065s(br) cm^{-1}. NMR (CCl_4), Me_2Si δ —0.05(s); CH_3 1.08(t); CH_2O 3.40(q); CH_2 0.50(m), 1.50(t), 2.58(m); OH 3.10(s,br) ppm.

(ii) 1-Amino-3-[dimethyl(ethoxy)silyl]propane, [$Me_2(EtO)Si(CH_2)_3NH_2$] (IVb). Reaction of 3-dimethyl(ethoxy)silyl-*N,N*-bis(trimethylsilyl)propylamine (IIIb) and excess absolute ethanol gave the compound (96%), b.p. 60°C/8 mmHg, n_D^{18} 1.4186. (Found: C, 52.2; H, 11.7; N, 8.7%; mol. wt. 161. $C_7H_{19}NOSi$ calcd.: C, 52.2; H, 11.7; N, 8.7%; mol. wt. 161. $C_7H_{19}NOSi$ calcd.: C, 52.2; H, 11.8; N, 8.7%; mol. wt. (161). IR (liquid film), $\nu(NH_2)$, 3320m(br); ν(Me—Si), 1265s(sh), 850s(br); ν(Si—O—C), 1100s(br) cm^{-1}. NMR (neat), Me_2Si δ —0.10(s); CH_3 0.97(t); CH_2O 3.20(q); CH_2 0.40(m), 1.33(m), 2.43(t); NH_2 2.00(s) ppm.

(iii) 4-[Dimethyl(ethoxy)silyl]butyric acid, [$Me_2(EtO)Si(CH_2)_3CO_2H$] (IVc). A reaction, similar to that in F(i) between 3-[dimethyl(ethoxy)silyl]-*O*-trimethylsilylbutyrate (IIIc) and absolute ethanol, gave the desired product (80%), b.p. 64°C/1.5 mmHg, n_D^{18} 1.4165. (Found: C, 50.5; H, 9.5%; mol. wt. 190. $C_8H_{18}O_3Si$ calcd.: C, 50.5; H, 9.5%; mol. wt. 190). IR (liquid film), ν(C=O), 1750s; ν(Me—Si), 1265s, 850s; ν(Si—O—C), 1070s cm^{-1}. NMR (neat), Me_2Si δ 0.10(s); CH_3 1.00(t); CH_2O 3.36(q); CH_2 0.36(m), 1.50(m), 2.10(t); OH 12.10(s,br) ppm.

(iv) [p-Dimethyl(ethoxy)silyl]phenol, [p-$Me_2(EtO)SiC_6H_4OH$] (IXa). [*p*-Dimethyl(dimethylamino)silyl]phenoxytrimethylsilane (VIIIa) and absolute ethanol as in F(i) gave the product (90%), m.p. 30—31°C ($CHCl_3$—pet. ether). (Found: C, 61.1; H, 8.3%; mol. wt. 196. $C_{10}H_{16}O_2Si$ calcd.: C, 61.2; H, 8.2%; mol. wt. 196). IR (nujol), ν(OH), 3415m(br); ν(aromatic C—H), 1600s(sh); ν(Me—Si), 1275s, 845s; ν(*p*-subst.), 810s cm^{-1}. NMR ($CDCl_3$—DMSO), Me_2Si δ —0.05(s); CH_3 1.00(t); CH_2O 1.50(m); Ph 7.00(m); OH 9.00(s,br) ppm.

(v) p-Aminophenyl[dimethyl(ethoxy)]silane, [p-$Me_2(EtO)SiC_6H_4NH_2$] (IXb). *p*-[*N,N*-Bis(trimethylsilyl)aminophenyl]dimethyl(dimethylamino)silane (VIIIb) and absolute ethanol gave the compound (85%), b.p. 80°C/0.005 mmHg, n_D^{22} 1.4855. (Found: C, 62.4; H, 8.7; N, 7.2%; mol. wt. 195. $C_{10}H_{17}NOSi$ calcd.: C, 62.4; H, 8.9; N, 7.3%; mol. wt. 195). IR (liquid film), $\nu(NH_2)$, 3380s(br); ν(aromatic C—H), 1610s; ν(Me—Si), 1270s(sh), 850s; ν(*p*-subst.),

810s cm^{-1}. NMR (CCl_4), Me_2Si δ 0.00(s); CH_3 0.97(t); CH_2O 1.38(m); NH_2 2.80(s); Ph 7.10(m) ppm.

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