

DIFUNCTIONAL SILARYLENE-CONTAINING ALIPHATIC COMPOUNDS. SYNTHESIS AND CHARACTERIZATION OF BIS(*p*-(CARBOXYMETHYL)PHENYL)(*R*)PHENYLSILANE AND BIS(*p*-(2-AMINOETHYL)PHENYL)(*R*)PHENYLSILANE (R = Me, Ph)

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ABSTRACT

This work describes the synthesis of aliphatic diacids and diamines containing a silarylene moiety in the structure. These compounds can be employed as monomers for the synthesis of poly(amides) and poly(esters) or other condensation polymers. Thus, bis(*p*-methylphenyl)(*R*)phenylsilanes were obtained from *p*-bromotoluene and dichloro(*R*)phenylsilane (R= Me, Ph). Also, the dibenzyl nitrile compounds bis(*p*-(cyanomethyl)phenyl)(*R*)phenylsilanes were synthesized from the respective bis(*p*-(bromomethyl)phenyl)(*R*)phenylsilanes derivatives. The hydrolysis of the dibenzyl nitrile derivatives gives the respective diacids bis(*p*-(carboxymethyl)phenyl)(*R*)phenylsilanes with low yield. A direct Grignard reaction type was also studied using as precursors the dibenzyl bromide compounds. In a second stage, the synthesis of the phenethylamine bis(*p*-(2-aminoethyl)phenyl)(*R*)phenylsilane was studied by the reduction of the dibenzyl nitrile compounds. All compounds were characterized by IR-TF, ¹H, ¹³C and ²⁹Si NMR.

Keywords: Silicon, silarylene, dibenzyl bromide, dibenzyl nitrile, diphenylacetic acid, phenethylamines

INTRODUCTION

The route for synthesizing diphenylacetic acids and phenethylamines containing silicon as central atom in their structure has been employed by some authors with tolyl derivatives as the initial material. In this sense, Frankel et al.¹ prepared a series of silicon-containing phenethylamine derivatives: *p*-triethylsilylphenethylamine, *p*-trimethylsilylmethyl phenethylamine and D,L-1-*p*-trimethylsilylmethylphenyl-2-aminopropane from triethyl-*p*-tolylsilane. On the other hand, Migdal et al.² synthesized bis(*o*-(carboxymethyl)phenyl)dimethylsilane in order to prepare thermoplastic poly(esters) of low molecular weight by interfacial polymerization. The *p*-carboxymethylene isomer also was prepared^{2,3} and together with bis(*p*-(hydroxymethyl)phenyl)dimethylsilane⁴ was employed to prepare several poly(urethanes), poly(carbonates) and poly(esters). Other silicon-containing aliphatic difunctional compounds based on Ar-Si(CH₃)₂-Ar moiety were prepared by Rotman et al.³: bis(*p*-(formylphenyl)dimethylsilane, by hydrolysis of the respective dibenzyl bromide, and bis(*p*-(2-hydroxyethyl)phenyl)dimethylsilane, by reduction of the corresponding diphenylacetic acid. Later, a patent⁵ appeared where similar silicon-containing derivatives were synthesized, including bis(*p*-(dibromomethyl)phenyl)dimethylsilane, bis(*p*-(chlorocarbonylmethyl)phenyl)dimethylsilane, and bis(*p*-(*N*-methylcarbamoylmethyl)phenyl)dimethylsilane.

Kim et al.⁶ worked on compounds containing the Ar-Si(Ph)₂-Ar, Ar-Si(Me)(ⁿHex)-Ar or Ar-Si(ⁿBu)₂-Ar unit. The authors synthesized the series of bis(*p*-tolyl), dibenzyl bromides and dibenzyl triphenylphosphonium salt derivatives from *p*-bromotoluene, in order to obtain poly(*p*-phenylenevinylene)-related polymers.

Silicon-containing aromatic compounds have been synthesized, characterized and employed as monomers of polycondensation materials. Thus, it is possible to find structures based on bis(*p*-hydroxyphenylene)⁷⁻¹³, bis(*p*-bromophenylene)¹⁴, bis(aminophenylene)meta and para isomers,^{10,14-16} and bis(*p*-carboxyphenylene)^{11,17,18}, bis(*p*-ch orcarbonylphenylene)^{11,17-21}, bis(*p*-carboxyalkylphenylene)^{20,22}, bis(*p*-(3,4-dicarboxyphenylene))dianhydride^{16,23-26}, bis(*p*-isocyanatephenylene)²⁷, bis(*p*-carbohydrazidophenylene)²², bis(*p*-acidazidephenylene)¹⁴ and bis(*p*-chloroformatephenylene)^{13,28} moieties.

The several polymers obtained from these aromatic monomers show low chain-mobility with low to moderate glass transition temperatures (T_g). On the other hand, the solubility of these polymers in common organic solvents is strongly limited. Therefore, the incorporation of two methylene units in the new monomers and consequently in the repetitive unit of the polymers could be a positive factor in decreasing T_g while increasing the solubility of the materials without loss of the mechanical properties or great decrease of the thermal decomposition temperature (TDT). So, the next step of this work will be the synthesis of poly(esters), poly(amides), poly(imides) and/or polymer with combinations of these organic functions, containing monomers with and without methylene units as flexible elements.

EXPERIMENTAL PART

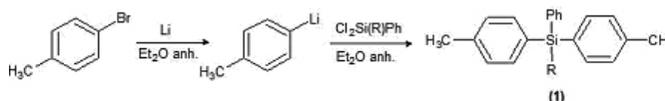
Materials

N-Bromosuccinimide (NBS), benzoyl peroxide (BPO), sodium cyanide, lithium aluminium hydride (LiAlH₄), diethylene glycol (DEG), tetrabutylammonium bromide (TBAB) and PhSi(R)Cl₂ (R= Me, Ph) were obtained from Aldrich Chemical (Milwaukee, WI) and used without further purification. Tetrahydrofuran (THF) and diethyl ether (Aldrich Chemical, Milwaukee, WI) were dried over sodium previously to use. All the reagents and solvents were purchased commercially as analytical-grade and used without further purification.

Instrumentation

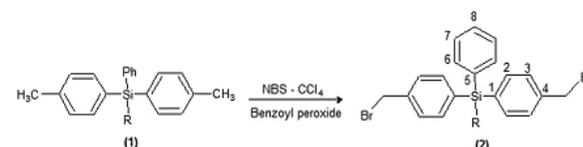
The IR spectra (KBr pellets) were recorded on a Perkin-Elmer (Fremont CA) 1310 spectrophotometer over the range of 4000-450 cm⁻¹. Melting points (uncorrected) were obtained on a SMP3 Stuart Scientific melting point apparatus. ¹H, ¹³C and ²⁹Si NMR spectra were carried out on a 400 MHz instrument (Bruker AC-200) using CDCl₃ as solvent and TMS as the internal standard.

Synthesis of precursors and monomers Bis(*p*-methylphenyl)(*R*)phenylsilanes (1)



Bis(*p*-methylphenyl)(*R*)phenylsilane (**1a**:R=Me, **1b**:R=Ph) derivatives were obtained according to the following procedure:^{11,29,30} A solution of *p*-bromotoluene (0.163 mol) in Et₂O anh. was slowly added over a mixture of Li (0.40 mol) and Et₂O anh. The *p*-tolyl lithium solution was refluxed for 2.5 h, cooled at 0 °C and then added the solution of the respective dichloro(*R*)phenylsilane (8x10⁻² mol) in anh. Et₂O. The system was refluxed for 4 h, cooled at room temperature and a HCl aq. solution was added in order to destroy the main portion of the remainder Li. After filtration, the organic portion was washed with water, dried using anh. MgSO₄ and the solvent removed. The white solid obtained was recrystallized from ethanol and characterized.

Bis(*p*-(bromomethyl)phenyl)(*R*)phenylsilanes (2)

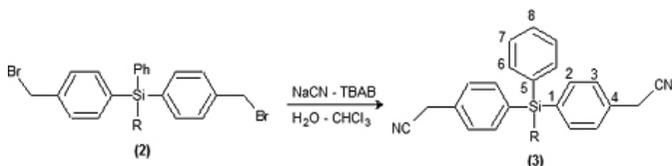


The dibenzyl bromide (**2a**:R=Me, **2b**:R=Ph) derivatives were synthesized according to a procedure described previously.^{5,6} This reaction uses benzoyl peroxide (0.75 mol%) as radical initiating agent and NBS (0.016 mol) in 100 mL of CCl₄ under nitrogen atmosphere. The mixture was heated and a solution of the respective bis(*p*-methylphenylene)(R)phenylsilane (8x10⁻² mol) in CCl₄ was slowly added. The system was refluxed for 6 h and then stirred at room temperature during 24 h. After cooling, the remainder NBS was removed by filtration and the solution was washed with water. The organic portion was treated with anh. CaCl₂, filtered and the solvent was removed by distillation. The white solid obtained was used without further purification due to its high spectroscopic purity.

Bis(*p*-(bromomethyl)phenylene)methylphenylsilane (2a): Yield 32%, mp 120-122 °C. IR (KBr) (n) (cm⁻¹): 3067 (C-H arom.), 2957, 2928 (C-H aliph.), 1598, 1503 (C=C arom.), 1426, 1109, 726 (silyl-Ph), 1228, 787 (silyl-CH₃), 832, 700 (arom. *p*-subst.), 745 (arom. mono-subst.), 605 (C-Br). ¹H NMR (CDCl₃) (d) (ppm): 0.86 (s,3H,Si-CH₃), 4.52 (s,4H,CH₂), 7.24-7.68 (m,13H,Ph-H). ¹³C NMR (CDCl₃) (d) (ppm): -3.39 (Si-CH₃), 33.3 (CH₂), 120.0 (C7), 129.7 (C3), 129.7 (C8), 134.3 (C6), 135.6 (C2), 136.4 (C5), 137.0 (C1), 139.1 (C4). ²⁹Si NMR (CDCl₃) (d) (ppm): -10.8.

Bis(*p*-(bromomethyl)phenylene)diphenylsilane (2b): Yield 38%, mp 211-214 °C. IR (KBr) (n) (cm⁻¹): 3066 (C-H arom.), 2957, 2916 (C-H aliph.), 1484, 1427 (C=C arom.), 1395, 1108, 726 (silyl-Ph), 785, 700 (arom. *p*-subst.), 737 (arom. mono-subst.), 606 (C-Br). ¹H NMR (CDCl₃) (d) (ppm): 4.52 (s,4H,CH₂), 7.21-7.72 (m,18H,Ph-H). ¹³C NMR (CDCl₃) (d) (ppm): 33.3 (CH₂), 125.9 (C7), 128.0 (C3), 125.8 (C8), 129.9 (C6), 130.2 (C2), 134.5 (C5), 136.3 (C1), 139.2 (C4). ²⁹Si NMR (CDCl₃) (d) (ppm): -14.3.

Bis(*p*-(cianomethyl)phenylene)(R)phenylsilanes (3)



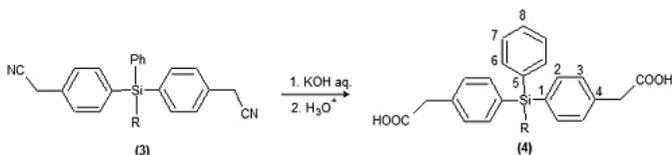
These syntheses were developed following classic references for phase-transfer reactions³¹. Sodium cyanide (0.10 mol) and TBAB (1x10⁻² mol) were dissolved in 40 mL of water. The solution was stirred for 15 min. at a temperature close to 50 °C. Later, the mixture was cooled at room temperature and 5x10⁻² mol of the respective dibenzyl bromide derivative dissolved in 20 mL of CHCl₃ was added. The systems was refluxed for 2 h and then cooled. Three portions of water were used for removing salts and the organic portion was treated with anh. CaCl₂. After filtration the solvent was removed and the crude product was dried at 50 °C during 12 h.

3b (R = Ph) was successively recrystallized from ethanol in order to obtain a white solid, while **3a** (R = Me) was dissolved in *n*-hexane and purified by chromatographic techniques using silica gel (Merck, 70-230 mesh) and a mixture of *n*-hexane/ethyl acetate (90/10 vol/vol) as eluent.

Bis(*p*-(cianomethyl)phenylene)methylphenylsilane (3a): Yield 38%, mp 35-38 °C. IR (KBr) (n) (cm⁻¹): 3068 (C-H arom.), 2959 (C-H aliph.), 2250 (CN), 1599, 1427 (C=C arom.), 1395, 725 (silyl-Ph), 1257, 784 (silyl-CH₃), 799, 699 (arom. *p*-subst.), 725 (arom. mono-subst.). ¹H NMR (CDCl₃) (d) (ppm): 0.83 (s,3H,Si-CH₃), 3.69 (s,4H,CH₂), 7.28-7.58 (m,13H,Ph-H). ¹³C NMR (CDCl₃) (d) (ppm): -3.38 (Si-CH₃), 23.6 (CH₂), 117.8 (CN), 127.6 (C7), 128.2 (C8), 128.8 (C4), 129.9 (C3), 131.5 (C1), 135.2 (C2), 135.9 (C5), 136.1 (C6). ²⁹Si NMR (CDCl₃) (d) (ppm): -10.6.

Bis(*p*-(cianomethyl)phenylene)diphenylsilane (3b): Yield 47%, mp 137-139 °C. IR (KBr) (n) (cm⁻¹): 3067 (C-H arom.), 3025, 2915 (C-H aliph.), 2250 (CN), 1598, 1427 (C=C arom.), 1415, 1109, 726 (silyl-Ph), 799, 702 (arom. *p*-subst.), 737 (arom. mono-subst.). ¹H NMR (CDCl₃) (d) (ppm): 3.76 (s,4H,CH₂), 7.24-7.57 (m,18H,Ph-H). ¹³C NMR (CDCl₃) (d) (ppm): 23.6 (CH₂), 117.6 (CN), 127.5 (C7), 128.1 (C3), 129.9 (C8), 131.5 (C4), 133.2 (C5), 134.1 (C1), 136.5 (C6), 137.1 (C2). ²⁹Si NMR (CDCl₃) (d) (ppm): -14.4.

Bis(*p*-(carboxymethyl)phenylene)(R)phenylsilanes (4)

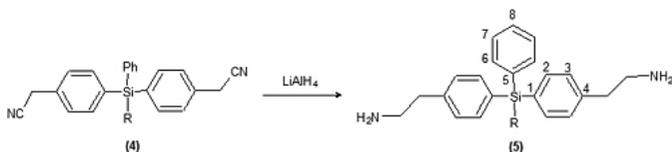


The preparation of diphenylacetic acid (**4a**:R=Me, **4b**:R=Ph) derivatives was realized following techniques already reported by Rotman et al. for dimethylsilane compounds³. Thus, 3x10⁻³ mol of the dibenzyl nitrile derivative was dissolved in 15 mL of DEG and the solution was heated at 40 °C during 30 min. Then 7 mL of aq. NaOH 50% solution was added and then refluxed at 90 °C for 48 h. After this, the system was cooled and aq. HCl (5%) solution was added until pH 1 was obtained. The organic portion was separated and washed with water and then treated with aq. NaOH 4% solution. The alkaline portion was acidified with aq. HCl and the crude product obtained was re-dissolved employing NaOH solution. A semi-solid of adequate spectroscopic purity was obtained after extracting with Et₂O, wash with water, dry with anh. MgSO₄ and distil the solvent.

Bis(*p*-(carboxymethyl)phenylene)methylphenylsilane (4a): Yield 37%. IR (KBr) (n) (cm⁻¹): 3396 (COO-H), 3069, 3045 (C-H arom.), 2958, 2922 (C-H aliph.), 1708 (C=O), 1599, 1427 (C=C arom.), 1397, 1109, 736 (silyl-Ph), 1402, 1251 (silyl-CH₃), 785, 700 (arom. *p*-subst.), 723 (arom. mono-subst.). ¹H NMR (CDCl₃) (d) (ppm): 0.82 (s,3H,Si-CH₃), 3.66 (s,4H,CH₂), 7.27-7.79 (m,13H,Ph-H), 10.0 (s,2H,COOH). ¹³C NMR (CDCl₃) (d) (ppm): -3.37 (Si-CH₃), 41.1 (CH₂), 127.9 (C7), 128.8 (C3), 128.9 (C8), 134.5 (C1), 134.9 (C5), 135.8 (C4), 136.4 (C2), 136.7 (C6), 177.5 (COOH). ²⁹Si NMR (CDCl₃) (d) (ppm): -10.8.

Bis(*p*-(carboxymethyl)phenylene)diphenylsilane (4b): Yield 41%. IR (KBr) (n) (cm⁻¹): 3404 (COO-H), 2995, 2980 (C-H arom.), 2941, 2875 (C-H aliph.), 1757 (C=O), 1523, 1400 (C=C arom.), 1377, 1158, 726 (silyl-Ph), 869, 717 (arom. *p*-subst.), 745 (arom. mono-subst.). ¹H NMR (CDCl₃) (d) (ppm): 3.55 (s,4H,CH₂), 7.18-7.61 (m,18H,Ph-H), 8.78 (s,2H,COOH). ¹³C NMR (CDCl₃) (d) (ppm): 41.3 (CH₂), 128.0 (C7), 128.1 (C1), 129.1 (C3), 129.8 (C8), 134.1 (C5), 135.3 (C4), 136.5 (C6), 136.8 (C2), 177.0 (COOH). ²⁹Si NMR (CDCl₃) (d) (ppm): -14.5.

Bis(*p*-(aminomethyl)phenylene)(R)phenylsilanes (5)



The phenethylamine (**5a**:R=Me, **5b**:R=Ph) derivatives were synthesized by reduction of the dibenzyl nitrile compounds according to described procedures^{1,3}. Thus, 5x10⁻² mol of the respective bis(*p*-(cianomethyl)phenylene)(R) phenylsilane was dissolved in 70 mL of THF and placed in a water-ice bath. Then a solution of 3x10⁻² mol of LiAlH₄ in 100 mL of THF was slowly added. The system was refluxed for 4 h and then stirred at room temperature during 12 h. After this, the system was cooled at 0 °C and 5 mL of water were added with stirring for 1 h. After filtration, the solution was treated with anh. CaCl₂ and the solvent removed by distillation.

Bis(*p*-(aminomethyl)phenylene)methylphenylsilane (5a): Yield 58%. IR (KBr) (n) (cm⁻¹): 3373 (N-H), 3066, 3011 (C-H arom.), 2954, 2851 (C-H aliph.), 1599, 1427 (C=C arom.), 1394, 1109, 726 (silyl-Ph), 1394, 1252 (silyl-CH₃), 784, 699 (arom. *p*-subst.), 723 (arom. mono-subst.). ¹H NMR (CDCl₃) (d) (ppm): 0.93 (s,3H,Si-CH₃), 1.97 (s,4H,NH₂), 2.68-2.80 (t,4H,Ph-CH₂), 2.82-3.00 (t,4H,CH₂-N), 7.14-7.78 (m,13H,Ph-H). ¹³C NMR (CDCl₃) (d) (ppm): -3.00 (Si-CH₃), 40.1 (Ph-CH₂), 43.4 (CH₂-N), 127.6 (C3), 128.6 (C7), 129.5 (C8), 132.8 (C1), 135.4 (C2), 136.2 (C6), 139.7 (C5), 141.2 (C4). ²⁹Si NMR (CDCl₃) (d) (ppm): -10.6.

Bis(*p*-(aminomethyl)phenylene)diphenylsilane (5b): Yield 55%. IR (KBr) (n) (cm⁻¹): 3359 (N-H), 3067, 3011 (C-H arom.), 2919, 2851 (C-H aliph.), 1599, 1428 (C=C arom.), 1393, 1108, 726 (silyl-Ph), 803, 701 (arom. *p*-subst.), 745 (arom. mono-subst.). ¹H NMR (CDCl₃) (d) (ppm): 2.12 (s,4H,NH₂), 2.72-2.79 (t,4H,Ph-CH₂), 2.80-3.01 (t,4H,CH₂-N), 7.12-7.76 (m,18H,Ph-H). ¹³C NMR (CDCl₃) (d) (ppm): 39.9 (Ph-CH₂), 43.2 (CH₂-N), 127.8 (C3), 128.5 (C7),

128.8 (C8), 134.4 (C1), 136.4 (C2), 136.8 (C6), 139.8 (C5), 141.2 (C4). ^{29}Si NMR (CDCl_3) (d) (ppm): -14.4.

RESULTS AND DISCUSSION

Difunctional silarylene-containing compounds were synthesized from *p*-bromotoluene and $\text{Cl}_2\text{SiCH}_3\text{Ph}$ or $\text{Cl}_2\text{Si}(\text{Ph})_2$ as starting materials. Thus, the bis(*p*-tolyl) derivatives were converted into the respective dibenzyl bromides by reaction with NBS and BPO. Later, the dibenzyl nitriles were obtained by reaction of the bromide compounds with NaCN and then hydrolyzed or reduced in order to prepare the diphenylacetic acids or the respective phenethylamines.

The synthesis and spectroscopic characteristics of bis(*p*-methylphenylene) derivatives (**1**) were already described^{11,29,30}. In these procedures we obtained high final yields using a 20%-mol of lithium excess in the *p*-methylphenyllithium preparation: 77% (**1a**) and 82% (**1b**). After recrystallization from ethanol the white solids showed a narrow melting point interval (82-83 °C and 118-119 °C for R= Me and Ph, respectively).

The synthesis of the dibenzyl bromide compounds (**2**) followed the Wohl-Ziegler methodology^{5,6}, which uses radical reactions promoted by PBO and NBS. The general route starting from bis(*p*-methylphenylene)methylphenylsilane and bis(*p*-methylphenylene)diphenylsilane is shown in figure 1.

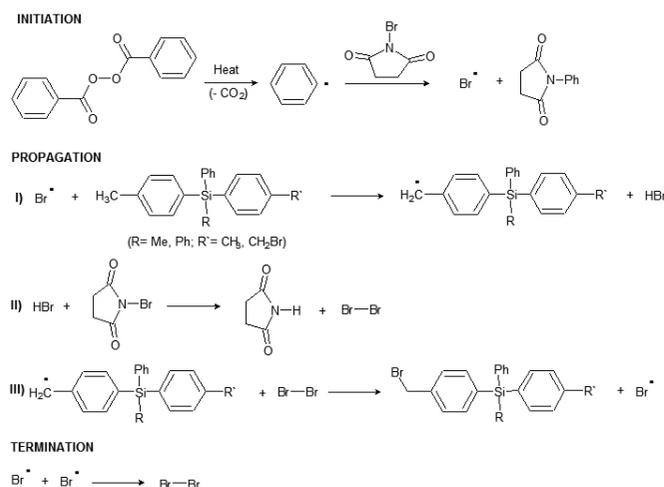


Figure 1. Synthesis of bis(*p*-(bromomethyl)phenylene)(R)phenylsilane derivatives using NBS.

In this reaction, the mixture time between BPO and NBS before adding the respective bis(*p*-tolyl) derivative (**1**) should ensure the formation of bromine radical and minimize the formation of molecular bromine. According with our observations, the optimal condition is accompanied by a change in the color of the system from yellow to light-orange. In both reactions the yields are below 40%; however, when we increase the mixture time, lower yields are obtained. These results agree with the general conclusion: the yield of reaction is strongly dependent on this initial mixture time.

The isolation procedure allows obtaining crude yellow-solids, which were purified by repeated treatment with Et_2O . Thus, white solids were characterized by their melting points: near 120 °C for the methyl derivative (**2a**) and 212 °C for the phenyl compound (**2b**). On the other hand, the IR-FT spectroscopic results showed common bands for bis(*p*-methylphenylene) derivatives, standing out the C-Br stretching band at 605 cm^{-1} (Table 1). IR and ^1H NMR data for bis(*p*-(bromomethyl)phenylene)diphenylsilane (**2b**) were already reported by Kim et al.⁵. Our characterization for this compound includes ^{13}C and ^{29}Si NMR data (Experimental Part).

The disappearance of the signal at 2.3 ppm related with the methyl group from *p*-tolyl derivatives and the appearance of a new signal at 4.5 ppm in the ^1H NMR spectrum is indicative of the formation of the $-\text{CH}_2\text{Br}$ group. A similar conclusion is obtained from ^{13}C NMR where the signal at 21.7 ppm is replaced by a new one at 33.3 ppm. It is clear that the silicon atom shields near the nuclei, so, the protons from the methyl group that is directly bonded to Si show a chemical shift of 0.86 ppm, while the carbon atom from same group appears at -3.39 ppm. This effect was possible to see in all spectra of the several compounds synthesized.

Table 1. Common and specific IR-FT spectroscopic bands (KBr, n, cm^{-1}) for silarylene-containing aliphatic compounds.

C-H arom.	2980-3070	
C-H aliph.	2850-3040	
C=C arom.	1600-1520	
Silyl-C arom.	1530-1400	
	1430-1380	
	1100-1160	
	725-740	
Silyl-C aliph. (R= CH ₃)	1200-1260	
	770-790	
Arom. <i>p</i> -subst.	780-870	
	700-720	
Arom. mono-subst.	720-740	
C-Br	605	Dibenzyl bromides (W= CH ₂ Br)
CN	2250	Dibenzyl nitriles (W=CH ₂ CN)
O-H	3390-3400	Diphenyl acetic acids (W=CH ₂ CO ₂ H)
C=O	1560-1700	
N-H	3350-3370	Phenethylamines (W= CH ₂ CH ₂ NH ₂)

For the synthesis of dibenzyl nitriles (**3a,b**) two general reaction conditions were developed using the dibenzyl bromide derivatives as starting materials. The direct cyanidation reaction agrees with reports⁵ using an ethanol-water mixture as solvent under different substrate-NaCN molar relation (1:3 and 1:6), temperature (40 and 90 °C) and time (2-96 h.), in the sense that do not promote obtaining of product. Due to this, phase-transfer conditions were developed using an organic solvent-water mixture and a phase transfer catalyst³¹. The solvents were CCl_4 , CH_2Cl_2 , Et_2O , hexane, toluene and CHCl_3 while tetrabutylammonium bromide (TBAB) and hexadecyltributylphosphonium bromide were used as transfer agent. Also, the time and molar relation between the substrate and NaCN were studied. The reaction optimal conditions were found for CHCl_3 , TBAB and a molar relation near 1:20 for dibenzyl bromide:NaCN. The yields obtained, between 38-47%, agree with the specific nature of the substrate. If this relation between reagents is also used in the direct cyanidation reactions, the respective dibenzyl nitrile compounds are obtained. The main factor in the synthesis of these derivatives is the relation between substrate and NaCN.

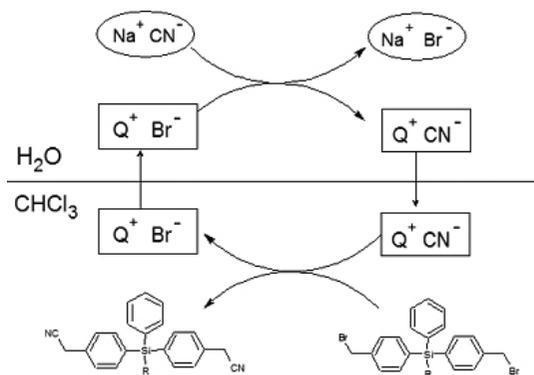


Figure 2. Synthesis of bis(*p*-(cyanomethyl)phenylene)(R)phenylsilane derivatives by phase-transfer process using tetrabutylammonium bromide ($\text{Q}^+ \text{Br}^-$).

The semi-solid crudes of brown color obtained from phase-transfer reactions can be purified by two methodologies: one is recrystallization from ethanol with great loss of mass because at least four processes are necessary to obtain white solids of high purity. The other method is to use a chromatographic technique. According to the different retention factors shown by dibenzyl bromides ($R_f=0.77$) and dibenzyl nitriles ($R_f=0.36$) in the SiO_2 -n-hexane/ethyl acetate (70/30 vol/vol) system, it was possible to isolate the products in good yields. The specific signals in the IR and NMR spectra are shown in Table 1.

The nitrile stretching band is the most important signal in the IR spectra and it appears at 2250 cm⁻¹. The NMR data show the displacement of the signal of the methylene group at high field due to the substitution of the bromine atom by the cyano group. On the other hand, for ¹³C NMR the nitrile carbon appears clearly at 117 ppm.

The synthesis of diphenylacetic acids (**4a,b**) was developed following two routes: The first included the use Grignard's techniques from the respective dibenzyl bromide (**2**). The second option was the direct basic hydrolysis of dibenzyl nitriles (**3**).

The Grignard reaction was employed by Kitamura et al.³² to obtain silicon-containing polymers. These authors reacted 2,7-dibromo-9,9-R₁R₂fluorenyl magnesium with several silicon-containing substrates. In our case, we tried to prepare the Grignard reagent from a silarylene compound and then add over CO₂. In spite of the experimental modifications carried out the results were not good. By using different anhydrous organic solvents, such as Et₂O and THF, several times and the reaction temperature employed in step 1 (0.5-10 h. and 20 °C-boiling point, respectively) or the use of iodine-crystal, do not promote the formation of the organo-magnesium intermediate. Due to these results, the basic hydrolysis of dibenzyl nitrile compounds was used to obtain the disalt first and then by acid treatment the respective diphenylacetic acid. For this purpose, we dissolved dibenzyl nitrile in ethanol and then added the aq. KOH solution³³. After the reaction and the isolation process, the yield was under 10%. When we replaced ethanol by diethyleneglicol, according to the Rotman et al. technique⁵, the yield obtained was better, but still very low (near 40%).

Although the product obtained after the re-precipitation in basic and then acid medium gives a semi-solid, this compound presents an appropriate spectroscopic purity. In Table 1 are summarized the principal bands found in the IR spectra, standing out the C=O and O-H stretching bands of carboxylic acid group near 1600 and 3400 cm⁻¹, respectively. The ¹H NMR spectrum of **4a** shows similar values for the methylene group while the **4b** compound shows a slight but clear displacement at low field. In both ¹³C NMR spectra no signals associated to the CN group was found and a new signal at 177 ppm appears (-COOH).

Finally, the reduction of dibenzyl nitrile compounds to obtain the respective phenethylamine was developed using LiAlH₄, in agreement with previous reports^{1,3}. The crude yields were moderate, with values near 60%. The phenethylamines (**5a,b**) were characterized without further purification because they decomposed on prolonged heating. The spectroscopic data show the characteristic signals for a primary amine: In the IR spectra it is possible to see the stretching bands associated to the N-H bond (Table 1). On the other hand, the ¹H NMR spectra show the -CH₂CH₂- unit with adequate chemical shifts, multiplicity and integration values. Likewise, the ¹³C NMR analyses show two methylene groups with displacements according with their electronic environments; CH₂-NH₂ appears to a lower field than the CH₂-Ph unit. The nature of methylene groups in all synthesized compounds was ratified by DEPT-135° analyses, whose results were not included in this work.

For all synthesized compounds: bis(*p*-tolyl), dibenzyl bromides, dibenzyl nitriles, diphenylacetic acids, and phenethylamines, the ²⁹Si NMR spectra show two environments for the silicon atom. When the silicon atom is bonded to phenyl groups only, their chemical shift is approximately -14.3 ppm. If a phenyl group is replaced by an aliphatic group such as the methyl group, the chemical shift appears at a lower field (approximately - 10.7 ppm). This effect was already reported by our group,¹³ whereby an electronic retrodonation could be taking place between the *p*-aromatic system and the silicon atom *d* orbital.

CONCLUSIONS

A series of difunctional aliphatic compounds containing a silarylene unit in their structure were synthesized and characterized: bis(*p*-methylphenyl)methylphenylsilane, bis(*p*-methylphenyl)diphenylsilane, bis(*p*-bromomethylphenyl)methylphenylsilane, bis(*p*-bromomethylphenyl)diphenylsilane, bis(*p*-cyanomethylphenyl)methylphenylsilane, bis(*p*-cyanomethylphenyl)diphenylsilane, bis(*p*-carboxymethylphenyl)methylphenylsilane, and bis(*p*-carboxymethylphenyl)diphenylsilane.

The cyanidation reaction of the dibenzyl bromide derivatives is especially sensitive to the concentration of NaCN. It is necessary to use the system near saturation, maintaining the molar proportion 1:20 for substrate:cyanide ion. On the other hand, the reduction reaction of the dibenzyl nitrile derivatives, allows to obtain the phenethylamines, bis(*p*-(2-aminoethyl)phenyl)methylphenylsilane and bis(*p*-(2-aminoethyl)phenyl)diphenylsilane, with yields of 58% and 55%, respectively. In all cases, the spectroscopic analyses of IR-FT, ¹H- and ¹³C-NMR clearly allowed to identify the structures.

For all the precursors and monomers ²⁹Si-NMR analyses were carried out.

The chemical displacements obtained evidence the different environments of the silicon atoms, whose magnitudes agree with the nature of the groups bonded to the heteroatom. Thus, for aliphatic groups the chemical displacement appears at lower field that that when the silicon atom is bonded to phenyl groups. For these latter substituents, it is possible to postulate an electronic retrodonation between the *p*-aromatic system and the silicon atom *d* orbital, which would shield the analyzed nucleus.

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