The investigation of a transsilylation reaction for the preparation of silyl esters: reactivity correlated with ^{29}Si NMR resonance frequencies

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Abstract

The investigation of a transesterification reaction involving silicon exchange (transsilylation) between a silyl ester and a chlorosilane is reported. The reaction studied involves an equilibrium interchange between trimethylsilyl benzoate and several chlorosilanes, as a preparation of various silyl esters and trimethylsilyl chloride as a volatile by-product. An interesting reactivity balance was observed, in which the reaction with some of the chlorosilanes required an initiating catalyst to proceed. A correlation between the ^{29}Si NMR chemical shifts of the chlorosilanes and their respective reactivities was observed. Chlorosilanes having ^{29}Si NMR chemical shifts greater than 31 ppm (referenced to tetramethylsilane standard at 0 ppm) required the use of a nucleophilic catalyst to initiate the reaction. Reaction of trimethylsilyl benzoate occurred without an initiator with chlorosilanes having ^{29}Si NMR chemical shifts of 5 to 19 ppm; for those resonating between 19 and 31 ppm, an initiator accelerated the reaction and gave improved yields of transsilylated product. N,N-Dimethylformamide and sodium iodide were found to be effective and convenient catalysts/initiators for the reaction. © 1997 Elsevier Science S.A.

Keywords: Transsilylation; Silyl ester; ^{29}Si NMR

1. Introduction

Degradable polymers are receiving a great deal of interest due to their current and potential biomedical applications [1] and increasing environmental concerns [2]. To generate materials for a broad range of applications, efforts have been directed toward obtaining control and variability over the degradation rates and the degradation properties of hydrolytically cleavable polymers. Poly(silyl ester)s [3] were recently reported as a new class of degradable polymeric materials, where variation in the susceptibility toward nucleophilic cleavage was accomplished through alteration of the substituents attached to the silicon atoms. These polymers were formed from the condensation transsilylation reaction between dichlorotetra-substituted disiloxanes and bis(trimethylsilyl) esters. Recent attempts [4] to expand this family of degradable polymers through the use of other monomers, for example the condensation of bis(trimethylsilyl)adipate with 1,6-bis(chlorodimethylsilyl)hexane, were unsuccessful.

Although several silicon exchange reactions have been reported [5], only a few specific examples of transsilylation reactions involving the synthesis of silyl esters can be found; chlorodimethylsilane [6,7] and chloromethyldimethylchlorosilane [8] have been reported to undergo a transsilylation reaction with trimethylsilyl esters. The lack of transsilylation reactivity for trialkyl-substituted [4] chlorosilanes with trimethylsilyl esters was believed to be due to the decreased electrophilicity of the silicon atom, in comparison to those chlorosilanes with oxygen, hydrogen, or chloromethyl substituents. Presumably, because of the relative inertness of the two reactants, a nucleophilic initiator is needed to attack either one or both of the silicon species [9,10] and displace chloride ion and/or carboxylate to allow the reaction to propagate. Therefore, the transesterification reaction between trimethylsilyl esters and chlorosilanes was further investigated to study a broader scope of the reaction and to determine catalysts/initiators to effect the silicon exchange reaction. In addition, a correlation between the reactivity of the chlorosilanes and their ^{29}Si NMR chemical shifts was observed.

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2. Results and discussion

The reaction of trimethylsilyl benzoate, 1, with various chlorosilanes was employed for the investigation of the transsilylation transesterification reaction (Scheme 1). Initially, the reaction of 1 with *tert*-butyldimethylsilyl chloride (TBDMSCl) was used to study possible catalysts, and to optimize the reaction conditions. In the absence of a catalyst, the reaction was found to proceed to ca. 10% conversion to *tert*-butyldimethylsilyl benzoate, 2, after heating in tetrahydrofuran (THF) at reflux for 48 h. However, with the addition of N,N-dimethylformamide (DMF), sodium iodide, or trialkylamine hydrochloride salts, the reaction reached almost 50% conversion (Table 1). DMF was found to be the most convenient catalyst. [1] Varying the amount of DMF from 1 to 10 mol% did not affect the reaction. Sodium iodide in acetonitrile worked equally as well, but the formation of insoluble sodium chloride and the discoloration of solution made it a less suitable catalyst. Trimethylamine hydrochloride and triethylamine hydrochloride effected the reaction, but also resulted in increasing amounts of benzoic acid (observed by ^{1}H NMR) over time. The benzoic acid most likely arose due to hydrolysis as a result of incomplete drying of the hydrochloride salts or perhaps through the cleavage of the silyl ester bonds by the ionic catalysts [12].

The presence of an equilibrium in the transsilylation reaction [6] was demonstrated through both the addition of and the removal of trimethylsilyl chloride during the reaction. The addition of trimethylsilyl chloride (1.2 equiv.) to the reaction mixture containing 1, *tert*-butyldimethylsilyl chloride, and DMF (1 mol%) in THF heated at reflux under argon resulted in a shift of the equilibrium toward the reactants, which was observed by ^{1}H NMR as a reduction from 41% to 26% yield of 2 after 1 h. Conversely, a reduction in the pressure of the system from 760 mmHg to 90 mmHg for 1 h allowed for the removal of trimethylsilyl chloride and a shift in the equilibrium toward products, observed as an increase in the conversion of 1 to 2 from 46% to 55%. The equilibrium position for this reaction appears to be at 45% conversion of 1 to 2, with the modest increases in product over time being due to the loss of trimethylsilyl chloride. Optimized reaction conditions include allowing 1 to react with *tert*-butyldimethylsilyl chloride in the presence of DMF (1 mol%) in tetrahydrofuran (THF) [2] heated at reflux under argon for 24 h, followed by removal of trimethylsilyl chloride under a reduced
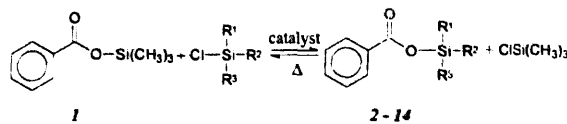
Scheme 1. General reaction scheme for the transsilylation reaction between trimethylsilyl benzoate and various silyl chlorides.

pressure of 80 mmHg at room temperature for 2 h, and then further heating of the reaction mixture for 24 h at 60 °C. Purification by distillation (99–102 °C at 2 mmHg) then gave 2 as a colorless liquid in 77% yield.

The progress of the transsilylation reactions between trimethylsilyl benzoate and various other silyl chlorides were also monitored by ^{1}H NMR. [3] As expected, the position of the equilibrium depended upon the reactivity of the silyl chloride. The observation that dimethylisopropylsilyl chloride and *tert*-butyldimethylsilyl chloride result in approximately the same conversions to dimethylisopropylsilyl benzoate, 3, and *tert*-butyldimethylsilyl benzoate, 2, respectively, while the equilibrium for dimethylphenylsilyl chloride lies much further toward products indicated that electronic effects play a substantial role in the transsilylation reaction. As additional support for the strong influence of electronic effects upon the transsilylation reaction, recall that the reaction of trialkyl-substituted silyl chlorides with trimethylsilyl esters requires the addition of a catalyst, while transsilylation occurs for 1,3-dichlorodisiloxanes [3], chlorodimethylsilane [6,7], and chloromethyldimethylchlorosilane [8] without the addition of a catalyst or initiator.

Because ^{29}Si NMR resonance frequencies are dependent upon both the steric and electronic effects of substituents attached to the silicon atoms [13–15], comparison of ^{29}Si NMR chemical shifts was useful in determining the reactivity of the silyl chlorides toward the transsilylation transesterification reaction. It is well known [13–15] that a parabolic relationship between chemical shift frequency and the sum of the electronegativities of the silicon substituents exists (Fig. 1). For the transsilylation reaction, each of the chlorosilanes studied is located in the upper portion of the parabola, where there is a great deal of scatter and a direct comparison between [29]Si chemical shift and substituent electronegativity is difficult. Our data do, however, seem to correlate quite well in the evaluation of the feasibility of the transsilylation reaction vs. [29]Si resonance frequency. It was found that silyl chlorides that react with trimethylsilyl benzoate without the addition of a catalyst resonate upfield from those silyl chlorides

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[1] DMF has previously been shown to act as a nucleophilic catalyst in the preparation of acid chlorides from SOCl₂ and carboxylic acids, see Ref. [11].

[2] THF solvent was required to prevent sublimation of the *tert*-butyldimethylsilyl chloride.

[3] In the preparation of 2, 3, and 4, removal of the lower-boiling trimethylsilyl chloride resulted in near completion of reaction and optimized isolated yields of the silyl ester products were 77%, 72% and 86% respectively.

Table 1

Comparison of the effects of the various catalysts upon the transesterification reaction between trimethylsilyl benzoate, 1, and tert-butyldimethylsilyl chloride in THF at reflux under argon, monitored as the formation of tert-butyldimethylsilyl benzoate, 2, by ^{1}H NMR (300 MHz, CDCl$_3$)

Time (h)	Conversion [a] (%)				
	1% DMF [b]	10% DMF [b]	1% Me$_3$NHCl [b]	1% Et$_3$NHCl [b]	NaI [c]
8	46	35	29	13	48
16	45	43	37	34	59
24	55	57	33	35	42
32	67	69	—	42	54
40	66	68	43	55	57

[a] Percentage conversion calculated from integration of the tert-butyl proton resonances of 2 at 1.02 ppm and comparison with the integration of the resonances of the aromatic protons at 7.4–7.6 and 8.0 ppm. Values given are the average percentage conversion for the reactions repeated in triplicate.

[b] Amounts of catalysts used are molar percentages.

[c] NaI reactions were done in acetonitrile.

that require a catalyst to undergo transsilylation. This is not surprising, considering that NMR resonances are dependent upon the electron density around the nucleus (taking into account the parabolic relationship between chemical shift and substituent electronegativity) and more electrophilic silyl chlorides should react more readily. The trialkyl silyl chlorides that require the addition of an initiator resonate downfield from TMSCl at 30.9 ppm. Except for the most highly reactive silyl chlorides (dichlorosilanes, 1,3-dichlorodisiloxanes and
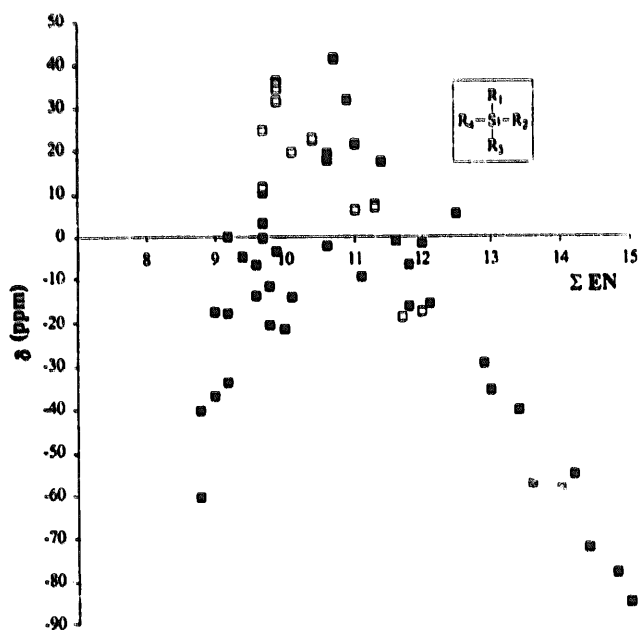

Fig. 1. Plot of ^{29}Si NMR chemical shifts vs. sum of substituent electronegativities [13,14]; ■ data points taken from reference [13]; □ measured chlorosilane chemical shifts with calculated [13,14] electronegativity values.

hydridochlorosilanes), the addition of a catalyst greatly improves the extent of reaction. For example, the ^{29}Si NMR shift of phenyldimethylsilyl chloride is at 19.9 ppm and the reaction with trimethylsilyl benzoate proceeds to 28% conversion to dimethylphenylsilyl benzoate, 4, after 24 h without the addition of an initiator. However, with the addition of 10% DMF, this reaction proceeds to 73% conversion after 24 h. It would be interesting to investigate the correlation between chemical shift and reactivity for chlorosilanes whose ^{29}Si resonances are at very high field and bearing the extreme of high- and low-electronegativity substituents; however, there are no appropriate chlorosilanes for the transsilylation reaction at either substituent-electronegativity extreme.

^{1}H nuclear magnetic resonance spectroscopy allowed for convenient monitoring and quantification of the extents of reactions, in which the ^{1}H NMR resonances for the protons of the silyl esters resonate downfield in comparison to the corresponding silyl chlorides. ^{13}C (75 MHz) and ^{29}Si INEPT [4] NMR spectroscopy were also useful in the characterization of the structure and purity of the products. In addition, any hydrolysis was observable by ^{1}H and ^{29}Si NMR. As expected, the silicon resonance frequencies shifted upfield, [14] upon transformation from the chlorosilane to the silyl ester.

In summary, a number of silyl esters have been prepared, incorporating commonly employed silicon units, by a mild and general transsilylation reaction. DMF was found to be an effective catalyst for the transsilylation of chlorosilanes lacking sufficient electrophilicity to undergo the transesterification reaction, and the reactivity of the chlorosilanes was found to correlate with ^{29}Si NMR resonance frequencies. This methodology is currently being applied to the syntheses of poly(silyl ester)s [4].

3. Experimental section

3.1. General directions

All manipulations of reagents and reactions were performed under argon. ^{1}H NMR spectra were recorded on a Varian Unity-plus (300 MHz) spectrometer with the solvent proton signal as standard. ^{13}C NMR spectra were recorded at 75 MHz on a Varian Unity-plus spectrometer with the solvent carbon signal as standard. ^{29}Si NMR spectra were recorded using standard INEPT

[4] Silicon was observed by standard INEPT (insensitive nuclei enhanced by polarization transfer) experiments, with coherence transfer from the protons of the alkyl or aryl substituents to the silicon, which gave enhanced sensitivity and resulted in excellent NMR spectra using small amounts of sample and few scans, see Ref. [16].

experiments [16] on a Varian Unity-plus spectrometer at 59.6 MHz and were referenced externally to tetramethylsilane at 0 ppm. IR spectra were obtained on a Mattson polaris spectrometer as thin films on NaCl disks. Elemental analyses were performed by Galbraith Laboratories or MHW Laboratories and are reported for purified and unpurified compounds. Mass spectrometry was provided by the Washington University Mass Spectrometry Resource, an NIH Research Resource (Grant No. P41RR0954). Owing to the susceptibility of these compounds toward nucleophilic cleavage [10], most of the compounds reacted with the MS matrices preventing correct MS analysis.

3.2. Materials

Silicon compounds were purchased from United Chemical Technology or Aldrich and were distilled prior to use. THF was distilled from Na–benzophenone. DMF was stirred over calcium oxide for 12 h, distilled under reduced pressure and stored over molecular sieves. CH_3CN was dried over and distilled from CaH_2. Trimethylamine hydrochloride and triethylamine hydrochloride were purchased from Aldrich and dried in a vacuum oven (120 °C) in the presence of phosphorus pentoxide. NaI was purchased from Aldrich.

3.3. Dimethylisopropylsilyl benzoate (3)

Trimethylsilyl benzoate (3.40 g, 17.5 mmol) and chlorodimethylisopropylsilane (4.73 g, 34.6 mmol) were added to a 25 ml flame-dried round bottom flask via tared syringe. DMF was added (0.10 ml, 1.3 mmol, 7.4%) via syringe. The reaction mixture was allowed to stir under an argon atmosphere at 100 °C for 2 days. The product was distilled at 116 °C at 8 mmHg. The yield of the product, which was a clear liquid, was 3.52 g, 15.9 mmol (91%). IR (neat) 3090–3030, 2950–2860, 1700, 1600–1575, 1490–1450, 1315–1255, 1175, 1116, 1068, 1026, 1002, 860–780, 711 cm⁻¹. ^{1}H NMR (300 MHz, CDCl₃) δ 0.37 (6H, s, -Si(CH₃)₂(CH(CH₃)₂)), 1.07 (6H, d, J = 6 Hz, =Si(CH₃)₂(CH(CH₃)₂)), 1.14 (1H, septet, J = 6 Hz, -Si(CH₃)₂(CH(CH₃)₂)), 7.44 (2H, t, J = 8 Hz, aromatic H), 7.53 (1H, t, J = 8 Hz, aromatic H), 8.05 (2H, d, J = 8 Hz, aromatic H) ppm. ^{13}C NMR (75 MHz, CDCl₃) δ −4.03 (-Si(CH₃)₂(CH(CH₃)₂)), 14.06 (-Si(CH₃)₂(CH(CH₃)₂)), 16.50 (-Si(CH₃)₂(CH(CH₃)₂)), 128.18 (aromatic C), 130.03 (aromatic C), 131.35 (ipso aromatic C), 132.79 (aromatic C), 166.52 (carbonyl C) ppm. ^{29}Si NMR IN-EPT (59.6 MHz, CDCl₃) δ 26.94 ppm. Anal. calcd. for C₁₂H₁₈O₂Si (222.36): C, 64.82%; H, 8.16%. Found: C, 64.98%; H, 7.96%. HRMS (FAB) calcd. for C₁₂H₁₈O₂Si (M + H⁺) 223.1154. Found 223.1157.

3.4. Triisopropylsilyl benzoate (5)

Trimethylsilyl benzoate (2.49 g, 12.8 mmol) and chlorotriisopropylsilane (2.74 g, 14.2 mmol) were added to a 25 ml flame-dried round bottom flask via tared syringe. DMF (0.10 ml, 1.3 mmol, 10%) was added via syringe. The reaction mixture was allowed to stir under an argon atmosphere at 100 °C for 10 days. The product was distilled at 175 °C at 11 mmHg. The yield of the product, which was a clear liquid, was 2.79 g, 10.0 mmol (78%). IR (neat) 2950–2870, 3130–3080, 1704, 1605–1580, 1463, 1451. 1313–1286, 1174, 1117, 1060, 1000, 870, 845, 740, 680 cm⁻¹. ^{1}H NMR (300 MHz, CDCl₃) δ 1.16 (18H, d, J = 7 Hz, -Si(CH(CH₃)₂)₃), 1.41 (3H, septet, J = 7 Hz, -Si(CH(CH₃)₂)₃), 7.44 (2H, t, J = 8 Hz, aromatic H), 7.55 (1H, t, J = 8 Hz, aromatic H), 8.08 (2H, d, J = 8 Hz, aromatic H) ppm. ^{13}C NMR (75 MHz, CDCl₃) δ 12.03 (Si(CH(CH₃)₂)₃), 17.83 (Si(CH(CH₃)₂)₃), 128.27 (aromatic C), 130.10 (aromatic C), 131.45 (ipso aromatic C), 132.79 (aromatic C), 166.23 (carbonyl C) ppm. ^{29}Si NMR IN-EPT (59.6 MHz, CDCl₃) δ 22.64 ppm. Anal. calcd. for C₁₆H₂₆O₂Si (278.47): C, 69.01%; H, 9.41%. Found: C, 69.23%; H, 9.30%. LRMS (FAB) calcd. (M + H⁺) 279.2. Found 279.2.

3.5. 1,6-Bis(benzoyldimethylsilyl)hexane (6)

Trimethylsilyl benzoate (1.42 g, 7.30 mmol) and 1,6-bis(chlorodimethylsilyl)hexane (1.26 g, 4.65 mmol) were added to a flame-dried 25 ml round bottom flask via tared syringe. DMF (0.02 ml, 0.3 mmol, 4%) was added to the flask via syringe. The reaction mixture was allowed to stir under an argon atmosphere at 70 °C for 3 days. The product could not be purified by distillation on a Büchi Kugelrohr distillation apparatus at 0.14 mmHg up to 250 °C. The approximate yield of the unpurified product, which was a viscous oil, was 1.04 g, 2.34 mmol (64%). IR (neat) 3090–3030, 2955–2855, 1708–1704, 1601–1575, 1490, 1451, 1408, 1313, 1295, 1280, 1257, 1175, 1026–1009, 900, 836, 711 cm⁻¹. ^{1}HNMR (300 MHz, CDCl₃) δ 0.36 (12H, s, (-Si(CH₃)₂CH₂CH₂CH₂-)₂), 0.85 (4H, t, J = 8 Hz, (-Si(CH₃)₂CH₂CH₂CH₂-)₂), 1.38 (8H, m, (-Si(CH₃)₂CH₂CH₂CH₂-)₂), 7.41 (4H, t, J = 7 Hz, aromatic H), 7.54 (2H, t, J = 7 Hz, aromatic H), 8.03 (4H, d, J = 7 Hz, aromatic H) ppm. ^{13}C NMR (75 MHz, CDCl₃) δ −17.3 ((-Si(CH₃)₂CH₂CH₂CH₂-)₂), 16.05 ((-Si(CH₃)₂CH₂CH₂CH₂-)₂), 22.74 ((-Si(CH₃)₂CH₂CH₂CH₂-)₂), 32.75 ((-Si(CH₃)₂CH₂CH₂CH₂-)₂), 128.23 (aromatic C), 130.09 (aromatic C), 131.37 (ipso aromatic C), 132.85 (aromatic C), 166.67 (carbonyl C) ppm. ^{29}Si NMR IN-EPT (59.6 MHz, CDCl₃) δ 24.98 ppm. Anal. calcd. for C₂₄H₃₄O₄Si₂ (442.70): C, 65.11%; H, 7.74%. Found: C, 64.17%; H, 8.35%.

3.6. Diisopropylsilyl benzoate (7)

Trimethylsilyl benzoate (2.88 g, 14.8 mmol) and chlorodiisopropylsilane (3.31, 21.9 g, mmol) were added to a 25 ml flame-dried round bottom flask via tared syringe. The reaction mixture was allowed to stir under an argon atmosphere at 100 °C for 24 h. The product was distilled at 157 °C at 6 mmHg. The yield of the product, which was a clear liquid, was 2.88 g, 12.2 mmol (83%). IR (neat) 3090–3030, 2930–2867, 2144, 1704, 1600–1580, 1462, 1452, 1380–1287, 1176, 1114, 1068, 1026, 1004, 881, 804, 761, 711 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.13 (12H, d, $J = 7$ Hz, –SiH(CH(CH_3)$_2$)$_2$), 1.25 (2H, d septet, $J = 7$ Hz, $J = 2$ Hz, –SiH(CH(CH$_3$)$_2$)$_2$), 4.58 (1H, t, $J = 2$ Hz, –SiH(CH(CH$_3$)$_2$)$_2$), 7.44 (2H, t, $J = 8$ Hz, aromatic H), 7.56 (1H, t, $J = 8$ Hz, aromatic H), 8.08 (2H, d, $J = 8$ Hz, aromatic H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ 11.79 (–SiH(C H(CH$_3$)$_2$)$_2$), 17.21 (–SiH(CH(CH$_3$)$_2$)$_2$), 128.32 (aromatic C), 130.18 (aromatic C), 131.02 (ipso aromatic C), 133.05 (aromatic C), 166.66 (carbonyl C) ppm. ^{29}Si NMR INEPT (59.6 MHz, CDCl$_3$) δ 15.21 ppm. HRMS (FAB) calcd. for C$_{13}$H$_{20}$O$_2$Si (M – H$^+$) 235.1154, found 235.1150.

3.7. Dimethylsilyl benzoate (9)

Trimethylsilyl benzoate (2.95 g, 15.2 mmol) and chlorodimethylsilane (11.99 g, 126.7 mmol) were added to a 25 ml flame-dried round bottom flask via tared syringe. The reaction mixture was allowed to stir under an argon atmosphere at room temperature for 10 days. The product was distilled on a Büchi Kugelrohr distillation apparatus at 100 °C at 11 mmHg. The product obtained, 2.47 g, 13.7 mmol (90%), was a clear liquid. IR (neat) 3040–3020, 2963–2900, 2150, 1700, 1600–1575, 1310, 1290, 1255, 1125, 1070, 907, 886, 770, 708 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.48 (6H, d, $J = 3$ Hz, –SiH(CH_3)$_2$), 4.99 (1H, septet, $J = 3$ Hz, –SiH(CH$_3$)$_2$), 7.42 (2H, t, $J = 8$ Hz, aromatic H), 7.55 (1H, t, $J = 8$ Hz, aromatic H), 8.06 (2H, d, $J = 8$ Hz, aromatic H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ –2.05 (–SiH(CH$_3$)$_2$), 128.21 (aromatic C), 130.10 (ipso aromatic C), 130.72 (aromatic C), 133.02 (aromatic C), 166.92 (carbonyl C) ppm. ^{29}Si NMR INEPT (59.6 MHz, CDCl$_3$) δ 7.70 ppm. Anal. calcd. for C$_9$H$_{12}$O$_2$Si (180.28): C, 59.96%; H, 6.71%. Found: C, 59.76%; H, 6.58%.

3.8. Dibenzoyltetraisopropyldisiloxane (10)

Trimethylsilyl benzoate (6.45 g, 33.2 mmol) and dichlorotetraisopropyldisiloxane (5.20 g, 16.5 mmol) were added to a 25 ml flame-dried round bottom flask via tared syringe. The reaction mixture was allowed to

stir under an argon atmosphere at 100 °C for 10 days. The product was collected at approximately 210 °C at 0.14 mmHg on a Büchi Kugelrohr distillation apparatus. The product was a clear liquid. The collected yield of the product was 6.60 g, 13.2 mmol (80%). IR (neat) 3090–3030, 2948–2870, 1709, 1580–1600, 1463, 1451, 1390, 1360, 1313, 1293, 1251, 1117–1061, 998, 885, 848, 761, 710 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.15 (24H, d, $J = 7$ Hz, Si(CH(CH_3)$_2$)$_2$), 1.40 (4H, septet, $J = 7$ Hz, Si(CH(CH$_3$)$_2$)$_2$), 7.38 (4H, t, $J = 8$ Hz, aromatic H), 7.54 (2H, t, $J = 8$ Hz, aromatic H), 8.04 (2H, d, $J = 8$ Hz, aromatic H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ 13.09 (Si(C H(CH$_3$)$_2$)$_2$), 16.83 (Si(CH(CH$_3$)$_2$)$_2$), 128.26 (aromatic C), 130.19 (aromatic C), 130.99 (ipso aromatic C), 132.92 (aromatic C), 165.55 (carbonyl C) ppm. ^{29}Si NMR INEPT (59.6 MHz, CDCl$_3$) δ –10.14 ppm. Anal. calcd. for C$_{26}$H$_{38}$O$_5$Si$_2$ (486.76): C, 64.16%; H, 7.87%. Found: C, 61.74%; H, 7.99%.

3.9. Dibenzoyltetramethyldisiloxane (11)

Trimethylsilyl benzoate (3.86 g, 19.87 mmol) and dichlorotetramethyldisiloxane (1.90 g, 9.34 mmol) were added to a flame-dried 25 ml round bottom flask via tared syringe. The reaction mixture was allowed to stir under an argon atmosphere at 70 °C for 3 days. The product was distilled in a Büchi Kugelrohr apparatus at ca. 195 °C at 0.14 mmHg. The yield of the product, which was a clear liquid, was 2.59 g, 6.92 mmol (74%). IR (neat) 3090–3030, 2960–2900, 1700, 1600–1575, 1490, 1410, 1287, 1266, 1176, 1115, 1069, 826, 753, 711 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.50 (12H, s, Si(CH_3)$_2$), 7.38 (4H, t, $J = 8$ Hz, aromatic H), 7.52 (2H, t, $J = 7$ Hz, aromatic H), 8.05 (4H, d, $J = 7$ Hz, aromatic H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ –0.39 (Si(CH$_3$)$_2$), 128.17 (aromatic C), 130.10 (aromatic C), 130.88 (ipso aromatic C), 130.95 (aromatic C), 165.88 (carbonyl C) ppm. ^{29}Si NMR INEPT (59.6 MHz, CDCl$_3$) δ –5.94 ppm. Anal. calcd. for C$_{18}$H$_{22}$O$_5$Si$_2$ (374.54): C, 57.72%; H, 5.92%. Found: C, 56.68%; H, 6.29%.

3.10. Dibenzoyldiphenylsilane (12)

Trimethylsilyl benzoate (4.70 g, 24.2 mmol) and dichlorodiphenylsilane (2.97 g, 11.7 mmol) were added to a 25 ml flame-dried round bottom flask via tared syringe. The reaction mixture was allowed to stir under an argon atmosphere at 70 °C for 14 days. The product could not be purified by distillation on a Büchi Kugelrohr distillation apparatus at 0.14 mmHg up to 250 °C. The unpurified product, which was a light brown viscous oil, was characterized. The approximate yield of the unpurified product was 3.00 g, 7.08 mmol (60%). IR (neat) 3080–3000, 1700, 1601–1584, 1489, 1451, 1430, 1314, 1289, 1280, 1175, 1128–1068 cm^{-1}. ^{1}H NMR

(300 MHz, CDCl₃) δ 7.44–7.64 (12H, m, aromatic H), 7.96 (4H, d, J = 7 Hz, aromatic H), 8.18 (4H, d, J = 8 Hz, aromatic H) ppm. ^{13}C NMR (75 MHz, CDCl₃) δ 128.10 (aromatic C), 128.43 (aromatic C), 130.17 (ipso aromatic C), 130.61 (aromatic C), 131.49 (ipso aromatic C), 133.50 (aromatic C), 133.71 (aromatic C), 135.28 (aromatic C), 165.20 (carbonyl C) ppm. ^{29}Si NMR IN-EPT (59.6 MHz, CDCl₃) δ −26.64 ppm. Anal. calcd. for C₂₆H₂₀O₄Si (424.53): C, 73.86%, H, 4.75%. Found: C, 71.49%; H, 4.72%.

3.11. Bis(dimethylamino)phenylsilyl benzoate (13)

Trimethylsilyl benzoate (4.47 g, 23.0 mmol) and bis(dimethylamino)chlorophenylsilane (6.68 g, 29.2 mmol) were added to a 25 ml flame-dried round bottom flask via syringe. The reaction mixture was allowed to stir under an argon atmosphere at 100 °C for 3 days. The product was distilled at 89–92 °C at 0.14 mmHg. The product obtained, 5.79 g, 18.4 mmol (80%), was a clear liquid. IR (neat) 3070–3000, 2880–2800, 1700, 1640, 1600, 1480, 1450, 1430, 1280, 1175–996, 846, 760–710 cm⁻¹. ^{1}H NMR (300 MHz, CDCl₃) δ 2.65 (12H, s, -Si(N(CH₃)₂)₂), 7.38–7.74 (8H, br m, aromatic H), 8.16 (2H, d, J = 7 Hz, aromatic H) ppm. ^{13}C NMR (75 MHz, CDCl₃) δ 37.48 (−Si(N(CH₃)₂)₂), 127.80 (aromatic C), 127.84 (aromatic C), 129.94 (aromatic C), 130.22 (aromatic C), 131.46 (ipso aromatic C), 132.60 (ipso aromatic C), 132.89 (aromatic C), 134.75 (aromatic C), 165.43 (carbonyl C) ppm. ^{29}Si NMR INEPT (59.6 MHz, CDCl₃) δ = −33.60 ppm. Anal. calcd. for C₁₇H₂₂O₂NSi (314.46): C, 64.93%; H, 7.05%. Found: C, 65.10%; H, 6.94%.

3.12. Dibenzoyltetraphenyldisiloxane (14)

Trimethylsilyl benzoate (2.63 g, 13.5 mmol) and dichlorotetraphenyldisiloxane (2.95 g, 6.54 mmol) were added to a 25 ml flame-dried round bottom flask via tared and heated syringe. The reaction mixture was allowed to stir under an argon atmosphere at 100 °C for 10 days. The product could not be purified by distillation at 0.14 mmHg up to 250 °C. The unpurified product, which was a very viscous oil, was characterized. The approximate yield of the unpurified product was 3.15 g, 5.06 mmol (77%). IR (neat) 3070–3000, 1700, 1600–1570, 1450, 1420, 1320, 1286, 1176, 1125–1074, 997, 934, 847, 772 cm⁻¹. ^{1}H NMR (300 MHz, CDCl₃) δ 7.30–7.52 (18H, br m, aromatic H), 7.83 (8H, d, J = 8 Hz, aromatic H), 7.95 (4H, d, J = 8 Hz, aromatic H) ppm. ^{13}C NMR (75 MHz, CDCl₃) δ 127.85

(aromatic C), 128.17 (aromatic C), 130.38 (aromatic C), 130.46 (ipso aromatic C), 130.80 (aromatic C), 131.46 (ipso aromatic C), 133.11 (aromatic C), 134.88 (aromatic C), 165.45 (carbonyl C) ppm. ^{29}Si NMR IN-EPT (59.6 MHz, CDCl₃) δ −35.04 ppm. Anal. calcd. for C₃₈H₃₀O₅Si₂ (622.82): C, 73.28%; H, 4.86%. Found: C, 71.10%; H, 4.95%.

Acknowledgements

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