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ONE-POT PREPARATION OF AROYLSILANES BY REDUCTIVE SILYLATION OF METHYL BENZOATES

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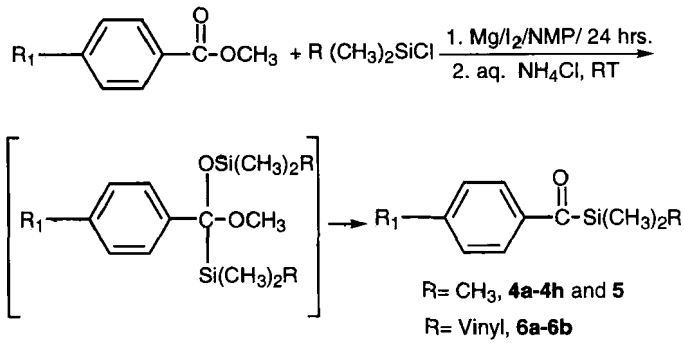
Abstract: A one-pot synthesis of aroylsilanes based on reductive silylation of methyl benzoates using Mg/ I_2/ chlorosilane in nontoxic 1-methyl-2-pyrrolidinone (NMP) solvent, is described. The yields are moderate to good and the method has been used for the preparation of some new bifunctional aroylsilanes.

Acylsilanes have attracted increasing interest since Brook first observed[1] that a carbonyl group located α to a silicon atom displays unusual reactivity. In recent years, acylsilanes have emerged as valuable building blocks for the syntheses of complex compounds due to their ability to undergo a variety of transformations.[2] Reductive silylation of alkyl benzoates with chlorosilane/ magnesium/ hexamethylphosphoric triamide (HMPT), followed by acidic hydrolysis, affords a synthetic method for aroyltrimethylsilanes, with direct use of commercially-available starting materials.[3] However, the use of HMPT is unpleasant because of its extreme toxicity and high cost.[3b,4] In connection with our ongoing project in exploring acylsilanes as synthons, we were interested in

developing a more convenient and versatile method based on an inexpensive and less toxic solvent. Based on the success in some synthetic applications,[5] we have now replaced HMPT with 1-methyl-2-pyrrolidinone (NMP), a nontoxic and less expensive solvent (see Scheme 1).



Scheme 1

Under similar conditions described by Picard, et. al.,[3] the reductive silylation of methyl benzoates did not take place in NMP solvent. We attempted to initiate the reaction by heating, but without success. However, under a catalytic amount of iodine activation the reaction proceeds well at room temperature. We also found that the silylation and hydrolysis can be carried out in one-pot under our conditions. Quenching of the reaction mixture and isolation of the silyl ketals as reported earlier[3] is not necessary before subsequent hydrolysis with aqueous HCl. Direct hydrolysis of the mixture resulting from reductive silylation with aqueous solution of ammonium chloride at room temperature gave the corresponding aroylsilanes in comparable yields to those previously reported; hydrolysis at 0 °C gives the corresponding silyl ketals. The reductive silylation seems to be very sensitive to the steric bulk of the chlorosilane used. Replacement of chlorotrimethylsilane by *tert*-butylchlorodimethylsilane or phenyl chlorodimethylsilane in the reaction gave no desired silyl ketals.

We have also extended this method for the preparation of aroylsilanes with additional functional groups, either on the silicon atom or on the aromatic ring. Based on this method, we were able to prepare *meta-* and *para-* methyl benzoate trimethylacylsilanes **4g**[6] and **4h**[7] respectively, 4-formylbenzoyl trimethylsilane **5**,[8] as well as benzoyl vinyl dimethylsilanes **6a**[9] and **6b**[10]. However, the yields for the methyl benzoate acylsilanes and vinyldimethylacylsilanes were low.

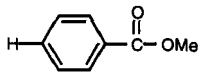
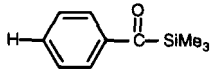
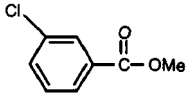
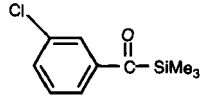
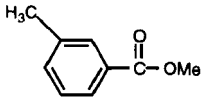
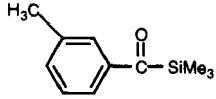
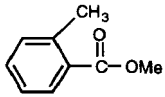
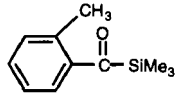
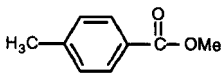
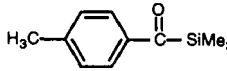
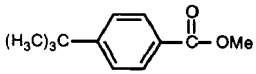
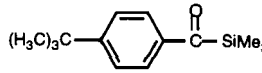
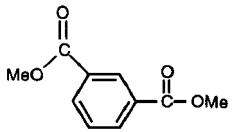
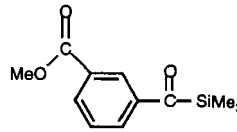
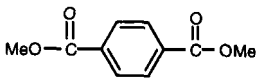
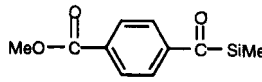
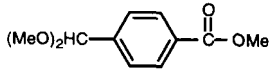
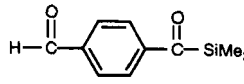
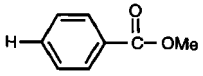
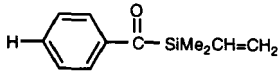
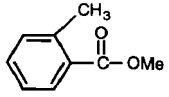
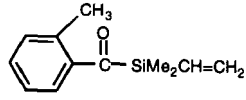
The results and isolated yields of the aroylsilanes are presented in **Table 1**. ^{13}C and ^{1}H NMR spectra of aroylsilanes **4a-4f** were in accordance with the assigned structures and literature data.[3b,11] In summary, we report a convenient method for the synthesis of aroylsilanes by reductive silylation of methyl benzoates using chlorosilane/ magnesium/ iodine/ 1-methylpyrrolidinone (NMP) in a one-pot procedure. The method has enabled us to synthesize some desired bifunctional aroylsilanes.

Experimental

^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ solutions on a Varian unity 300 (300 MHz) instrument. GC/MS data were obtained on a Hewlett Packard 5890 series instrument. HRMS data analyses were taken using chemical ionization, and analyses were done by the Southern California Mass Spectrometry Facility. Acidic ion-exchange resin, Dowex 50w x 8, and all benzoates except for **1i**, were commercially available. NMP and chlorotrimethylsilane were purchased from Aldrich in Sure-Seal bottles, and used without further purification. The protected aldehyde **1i** was synthesized following procedures by Neyer and Prakash.[12]

General Procedure for reductive silylation of methyl benzoates: Magnesium powder (0.05 mol, 1.2 g), iodine (0.8 mmol, 0.2 g), NMP (60 mL) and excess chlorotrimethylsilane (0.2 mol, 25 mL) were added and stirred for

Table 1. Preparation of Aroylsilanes

Entry	Substrate		Product	Yield[a] (%)
1a		4a		63
1b		4b		49
1c		4c		61
1d		4d		40
1e		4e		58
1f		4f		48
1g		4g		29
1h		4h		7
1i		5		52[b]
1a		6a		11
1d		6b		11

[a]isolated yield

[b]not very stable and decomposes into a white solid when left at rt

a few minutes before methyl benzoate (0.025 mol, 3.1 mL) was added dropwise. The reaction mixture was left stirring overnight at room temperature, and quenched with aqueous ammonium chloride. Hydrolysis at room temperature for one hour gave crude acylsilane directly after work-up, except for 3-chloro methyl benzoate **1b**, which gave a mixture of silylated ketals and the corresponding acylsilane.[13] During workup, some precipitate may form, which may be dissolved with addition of excess water prior to extraction. The organic layer was extracted with three 100-mL portions of pentane. The combined organic layers were dried over magnesium sulfate. Pentane was evaporated to give the crude product, which was purified through distillation and/or column chromatography.

Acknowledgment

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(4.) Zapp, J.A. Jr. *Science*, **1975**, 190.

(5.) Mg-promoted cross coupling of aldehydes, ketone, and esters with chlorotrimethylsilane in DMF has recently been reported. Ishino, Y., Maekawa, H., Takeuchi, H., Sukata, K. and Nishiguchi, I. *Chem. Lett.* **1995**, 829.

(6.) **4g:** ^{1}H NMR (δ): 0.37 (9H, s); 3.93 (3H, s); 7.54 (1H, td, J=8 Hz); 7.97 (1H, dt, J=8 Hz); 8.18 (1H, dt, J=8Hz); 8.49 (1H, td, J=2 Hz). ^{13}C (δ): -1.8 ($Si(CH_3)_3$); 52.1 (*m*-CO_2Me); 128.6, 128.7, 130.4, 130.7, 133.0, 141.0 (C_6H_4); 165.9 (*m*-CO_2Me); 234.4 ($COSiMe_3$). B.p./ mm Hg: 77-78 °C/ 0.2 mm Hg. Mass spectra, *m/z*: 236 (M^+, 4), 221 (18), 205 (11), 193 (36), 177 (30), 163(5), 104 (78), 73(100). HRMS, *m/z*: Found 237.0939 (MH^+); Calc. 237.0947 (MH^+).

(7.) **4h:** ^{1}H NMR (δ): 0.36 (9H, s); 3.92 (3H, s); 7.83 (2H, td, J=8 Hz); 8.12 (2H, td, J=8 Hz). ^{13}C (δ): -1.5 ($Si(CH_3)_3$); 52.4 (*p*-CO_2Me); 127.1, 129.9, 133.3, 143.9 (C_6H_4); 166.3 (*p*-CO_2Me); 235.9 ($COSiMe_3$). M.p. 43-44 °C. Mass spectra, *m/z*: 236 (M^+, 0.4), 235 (0.9), 221 (6), 205 (2), 193 (18), 177 (32), 163(3), 104 (37), 73(100). HRMS, *m/z*: Found 237.0956 (MH^+); Calc. 237.0947 (MH^+).

(8.) **5:** ^{1}H NMR (δ): 0.29 (9H, s); 7.87 (4H, d, J=9 Hz); 9.99 (1H, s). ^{13}C (δ): -1.8 ($Si(CH_3)_3$); 127.5, 129.9, 138.3, 144.5 (C_6H_4); 191.6 (*p*-COH); 235.9 (CO). Mass spectra, *m/z*: 206 (M^+, 18), 191 (7), 177 (39), 163 (55), 133 (6), 119 (2), 105 (9), 73 (100). HRMS, *m/z*: Found 207.0844 (MH^+); Calc. 207.0841 (MH^+).

(9.) **6a:** ^{1}H NMR (δ): 0.41 (6H, s); 5.87 (1H, dd, J_{trans}=20 Hz, J_{gem}=3 Hz); 6.12 (1H, dd, J_{cis}=15 Hz, J_{gem}=3 Hz); 6.36 (1H, dd, J_{trans}=20 Hz, J_{cis}=15 Hz); 7.41-7.51 (3H, m); 7.84 (2H, dt, J=7 Hz). ^{13}C NMR (δ): -3.5 ($Si(CH_3)_2$); 127.7, 128.5, 132.8, 134.4 (C_6H_4); 135.8, 141.3 ($CHCH_2$); 233.9 (CO). Mass spectra, *m/z*: 190 (M^+, 36), 189 (100), 175 (34), 163 (6), 147 (13), 135 (11), 121 (14), 105 (18), 85 (52), 77 (41), 59 (41), 51 (16). HRMS, *m/z*: Found 191.0889 (MH^+); Calc. 191.0892 (MH^+).

(10.) **6b:** ^{1}H NMR (δ): 0.36 (6H, s); 2.41 (3H, s); 5.83 (1H, dd, J_{trans}=20 Hz, J_{gem}=3 Hz); 6.09 (1H, dd, J_{cis}=15 Hz, J_{gem}=3 Hz); 6.29 (1H, dd, J_{trans}=20 Hz, J_{cis}=15 Hz); 7.18-7.32 (3H, m); 7.63 (1H, dd, J=7 Hz). ^{13}C NMR (δ): -3.7 ($Si(CH_3)_2$); 20.7 (*o*-CH_3); 125.7, 130.7, 131.9, 134.2 (m, C_6H_4); 135.6, 141.6 ($CHCH_2$); 239.7 (CO). Mass spectra, *m/z*: 204 (M^+, 12), 203 (16), 189 (100), 119 (31), 91 (36), 85 (83), 75 (22), 65 (21), 59 (90). HRMS, *m/z*: Found 205.1046 (MH^+); Calc. 205.1049 (MH^+).

(11.) **4a:** ^{1}H NMR (δ): 0.36 (9H, s); 7.42-7.54 (3H, m); 7.81 (2H, d, J=7 Hz). ^{13}C NMR (δ): -1.4 ($Si(CH_3)_3$); 235.7(CO). Mass spectra, *m/z*: 178 (M^+, 18), 105 (13), 73 (100).

4b: ^{1}H NMR (δ): 0.35 (9H, s); 7.36-7.48 (2H, m); 7.67-7.72 (2H, m). ^{13}C NMR (δ): -1.5 ($Si(CH_3)_3$); 234.3 (CO). Mass spectra, *m/z*: 214 (M+2, 0.5), 213 (M+1, 0.6), 212 (M^+, 1), 177 (23), 73 (100).

4c: ^{1}H NMR (δ): 0.34 (9H, s); 2.38 (3H, s); 7.30-7.36 (2H, m); 7.59-7.65

(2H, m). ^{13}C NMR (δ): -1.4 ($Si(CH_3)_3$); 21.3 (m-CH_3); 235.7 (CO). Mass spectra, *m/z*: 192 (M^+, 1), 91 (17), 73 (100).

4d: ^1H NMR (δ): 0.29 (9H, s); 2.39 (3H, s); 7.18-7.33 (3H, 7.53-7.56 (1H, m). ^{13}C NMR (δ): -1.7 ($Si(CH_3)_3$); 20.6 (o-CH_3); 242.2 (CO). Mass spectra, *m/z*: 192 (M^+, 8), 91 (15), 73 (100).

4e: ^1H NMR (δ): 0.34 (9H, s); 2.38 (3H, s); 7.25 (2H, d, J=8 Hz); 7.72 (2H, d, J=8 Hz). ^{13}C NMR (δ): -1.3 ($Si(CH_3)_3$); 21.7 (p-CH_3); 234.9 (CO). Mass spectra, *m/z*: 192 (M^+, 3), 91 (24), 73 (100).

4f: ^1H NMR (δ): 0.35 (9H, s); 1.32 (9H, s); 7.47 (2H, d, J=8 Hz); 7.78 (2H, d, J=8 Hz). ^{13}C NMR (δ): -1.3 ($Si(CH_3)_3$); 31.1, 35.5 ($C(CH_3)_3$); 234.8 (CO). Mass spectra, *m/z*: 234 (M^+, 1), 177 (100), 73 (65).

Also see Bernardi, F., Lunazzi, L., Ricci, A., Seconi, G. and Tonachini, G. *Tetrahedron*, **1986**, *42*, 3607. Olah, G.A., Berrier, A.L., Field, L.D. and Surya Prakash, G.K. *J. Am. Chem. Soc.*, **1982**, *104*, 1349.

(12.) Neyer, G. and Prakash, G. K. S. unpublished results. Methyl 4-formyl-benzoate (60 mmol, 10 g), trimethylorthoformate (70 mmol, 77 mL), and methanol (30 mL) were mixed with Dowex strongly acidic ion-exchange resin (1 g), which was prewashed with methanol and dried. The reaction mixture was refluxed for two hours, filtered and solvent evaporated. The resulting mixture was dissolved in ether (50 mL), and the solvent evaporated to yield colorless methyl-4-dimethoxyformyl-benzoate crystals.

(13.) Acetone (50 mL) was added to the reaction mixture after quenching with ammonium chloride. The aqueous solution was refluxed for two hours, and worked up similarly to give *m*- chloro acylsilane.

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