Supporting Information
for DOI: 10.1055/s-0036-1590835
© Georg Thieme Verlag KG Stuttgart · New York 2017
Formal Nucleophilic Silyl Substitution of Aryl Halides with Silyllithium Reagents via Halogenophilic Attack of Silyl Nucleophiles

Eiji Yamamoto, Satoshi Ukigai, Hajime Ito*

Division of & Frontier Chemistry Center, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan.

e-mail: hajito@eng.hokudai.ac.jp

Table of Contents

1. General and Materials S2
2. Experimental Procedures S2
3. References S5
4. $^1$H, $^{13}$C NMR Spectra S5
1. General and Materials

Materials were obtained from commercial suppliers and purified by standard procedures unless otherwise noted. Solvents for the reaction were also purchased from commercial suppliers, degassed via three freeze-pump-thaw cycles, and further dried over molecular sieves (MS 4A) prior to use if required. THF solutions of silyllithiums 2a, 2b and 2c were prepared according to the literature. The concentration of the silyllithium solution was confirmed by titration according to the Gilman’s method. Silyl substituted products 3aa, 3ba, 3ca, 3da, 3ea, 3fa, 3ha, 3ia, 3ka, 3la, 3ab, 3ac, 3ad, 3ad', 3ma, 3mb, 3mc, 3md, 3ma, 3mb, and (Z)- and (E)-3ma were identified by 1H NMR and comparison of GC retention time with the authentic samples prepared according to the Experimental Procedures in SI or the reported procedures. Analyses of the silyl substitution reactions with substrates 1f, 1g, and 1j were carried out using GC-MS. NMR spectra were recorded on JEOL JNM-ECX400P and ECS-400 spectrometer (1H: 400 MHz and 13C: 100 MHz). Tetramethylsilane (1H) and CDCl3 (13C) were employed as external standards, respectively. Multiplicity was reported as follows: s = singlet, brs = broad singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, quint = quintet, m = multiplet. Mesitylene was used as the internal standard for determining NMR yield. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with ULBON HR-1 glass capillary column (Shinwa Chemical Insudtries) and a FID detector. Diisopropylbenzene was used as the internal standard for determining GC yield. Recycle preparative gel permeation chromatography (GPC) was conducted with a JAI LC-9101 using CHCl3 as the eluent. NMR yields were detected from 1H NMR analysis of the crude mixture. High-resolution mass spectra (HRMS) were recorded at the Global Facility Center for Instrumental Analysis, Hokkaido University.

2. Experimental Procedures

2-1. Preparation of (TMS)3SiK

Tetrakis(trimethylsilyl)silane (160 mg, 0.5 mmol, 1.0 equiv) was placed in a vial with a screw cap containing a silicon-coated rubber septum, then it was connected to a vacuum/nitrogen manifold through a needle, and evacuated and refilled with nitrogen three times. The silane was dissolved with dry THF (2 mL). Then, a THF solution of K(O-t-Bu) (1.05 M solution, 500 µL, 0.525 mmol, 1.05 equiv) was added to the vial via syringe. After the resultant solution was stirred for 4 h at room temperature, solvent was removed under reduced pressure, and dry THF was added to the mixture to prepare 0.4 M (TMS)3SiK solution.

2-2. Procedure for Silyl Substitution Reaction with Silyllithium Reagent

A vial with a screw cap containing a silicon-coated rubber septum was connected to a vacuum/nitrogen manifold through a needle, and it was evacuated and refilled with nitrogen three
times. Dimethylphenylsilyllithium (0.4 M in THF, 2.0 equiv) was added to the vial under nitrogen atmosphere. After that, aryl halide (0.5 mmol) was added to the vial, then stirred at 30 ºC. After 1 h, the reaction mixture was analyzed by GC to check completeness of the reaction and the yields of products were determined by GC analysis or $^1$H NMR analysis of the crude reaction mixture.

2-3. Characterization of Silyl Substitution Products

Known arylsilanes $3_{aa}$, $3_{ba}$, $3_{ca}$, $3_{da}$, $3_{ea}$, $3_{ha}$, $3_{ia}$, and $3_{ka}$ were prepared according to the following typical procedures.

2-3. Typical Procedures for the Preparation of Authentic Arylsilane: (3,5-Dimethylphenyl)-dimethyl(phenyl)silane (3da)

Dimethylphenylsilyllithium (0.4 M in THF, 2.5 mL, 2.0 equiv) was added to the vial under nitrogen atmosphere. After that, 1-bromo-3,5-dimethylbenzene (93.5 mg, 0.51 mmol) was added to the vial, then stirred at 30 ºC. After 1 h, the reaction mixture was analyzed by GC to check the completeness of the reaction. After the reaction was completed, H$_2$O was added to the mixture, then, the extracted three times with Et$_2$O. The organic layer was washed with water. The combined organic layer was then dried over MgSO$_4$ followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography with hexane eluent, then further purified by GPC to give 3da in 63% isolated yield (76.5 mg, 0.318 mmol).

$^1$H NMR (392 MHz, CDCl$_3$, δ): 0.53 (s, 6H), 2.30 (s, 6H), 7.01 (s, 1H), 7.13 (s, 2H), 7.30-7.38 (m, 3H), 7.49-7.55 (m, 2H). $^{13}$C NMR (99 MHz, CDCl$_3$, δ): -2.3 (CH$_3$), 21.4 (C), 127.7 (CH), 129.0 (CH), 130.9 (CH), 131.9 (CH), 134.2 (CH), 137.1 (C), 137.9 (C), 138.5 (C). HRMS-EL (m/z): [M]+ calcd for C$_{16}$H$_{20}$Si, 240.13343; found, 240.13281.

[2-(But-3-en-1-yl)phenyl]dimethyl(phenyl)silane (3la).

A vial with a screw cap containing a silicon-coated rubber septum was connected to a vacuum/nitrogen manifold through a needle, and it was evacuated and refilled with nitrogen three times. 1-Bromo-2-(but-3-en-1-yl)benzene (105.5 mg, 0.50 mmol) and THF (0.32 mL) were added to the vial under nitrogen atmosphere. After that, the mixture was cooled to −78 ºC. n-BuLi (1.55 M,
0.32 mL) was added dropwise in syringe to the vial at –78 °C. After stirring 30 min, chlorodimethyl(phenyl)silane (85.5 mg, 0.50 mmol) was added dropwise. After 1 h, the reaction mixture was analyzed by GC to check the completeness of the reaction. After that, H₂O was added to the mixture, the extracted three times with Et₂O. The organic layer was washed with water. The combined organic layer was then dried over MgSO₄ followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography with hexane eluent, then further purified by GPC to give 3la in 73% isolated yield (97.7 mg, 0.367 mmol).

¹H NMR (392 MHz, CDCl₃, δ): 0.58 (s, 6H), 2.06–2.14 (m, 2H), 2.61–2.67 (m, 2H), 4.82–4.90 (m, 2H), 5.60–5.72 (m, 1H), 7.17–7.23 (m, 2H), 7.29–7.37 (m, 4H). ¹³C NMR (99 MHz, CDCl₃, δ): -0.90 (C₆H₃), 35.6 (C₆H₂), 36.0 (C₆H₂), 114.6 (C₆H₂), 125.2 (CH), 127.8 (CH), 128.7 (CH), 128.9 (CH), 134.0 (CH), 135.5 (CH), 136.0 (C), 138.0 (CH), 139.2 (C), 148.2 (C).

HRMS EI (m/z): [M–Me]+ calcd for C₁₇H₁₉Si, 251.12536; found, 251.12560.

2-5. Synthesis of [(2,3-Dihydro-1H-inden-1-yl)methyl]dimethyl(phenyl)silane (7).

A solution of 1H-indene (580.8 mg, 5.00 mmol) in dry THF (3.2 mL) was cooled to –78 °C, then n-BuLi (1.55 M in n-hexane, 5 mmol, 3.2 mL) was added dropwise to the solution. After stirring 30 min, (chloromethyl)dimethyl(phenyl)silane (923.6 mg, 5.00 mmol) was added dropwise to the solution. The resultant mixture was allowed to warm to room temperature and stirred for 19 h. The progress of the reaction was monitored by TLC. After the reaction was completed, H₂O was added to the mixture, the extracted three times with Et₂O. The organic layer was washed with water. The combined organic layer was then dried over MgSO₄ followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography. After that, the crude product (725.6 mg) and Pd/C (287.3 mg, 0.27 mmol) were dissolved in MeOH (2.7 mL). Then, the flask was connected a vacuum–H₂ balloon, and it was evacuated and refilled with hydrogen three times. The progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was concentrated and passed through a thin-pad of Celite. The resultant solution was evaporated and purified by silica-gel column chromatography with hexane eluent to give 7 in 40% isolated yield (535.8 mg, 2.01 mmol).

¹H NMR (392 MHz, CDCl₃, δ): 0.36 (d, J = 2.7 Hz, 6H), 0.92 (dd, J = 11.2, 14.8 Hz, 1H), 1.47–1.57 (m, 2H), 2.17–2.26 (ddt, J = 3.1, 7.5 12.2 Hz, 1H), 2.70–2.89 (m, 2H), 3.10–3.20 (m, 1H), 7.08–7.19 (m, 4H), 7.33–7.38 (m, 3H), 7.53–7.59 (m, 2H). ¹³C NMR (99 MHz, CDCl₃, δ): -2.2 (CH₃), -1.9 (CH₃), 21.8 (CH₂), 31.6 (CH₂), 35.1 (CH₂), 40.9 (CH), 123.0 (CH), 124.2 (CH), 126.0 (CH), 126.1
(CH), 127.8 (CH), 128.9 (CH), 133.5 (CH), 139.6 (C), 143.2 (C), 149.8 (C). HRMS-EI (m/z): [M]+
calcd for C_{18}H_{22}Si, 266.14908; found, 266.14862.

3. References

4. ^1^H, ^1^3C NMR Spectra
Author = element  
Experiment = single_pulse  
Sample_id = S#77772  
Solvent = CHLOROFORM-D  
Creation_time = 20-JAN-2016 19:13:59  
Revision_time = 20-JAN-2016 19:06:17  
Current_time = 20-JAN-2016 19:06:25  
Comment = single_pulse  
Data_format = 1D COMPLEX  
Dim_size = 13107  
Dim_title = 1H  
Dim_units = [ppm]  
Dimensions = X  
Site = EOX 400  
Spectrometer = JNM-ECS400  
Field_strength = 9.20197068[T] (390[MHz])  
X_acq_duration = 2.228224[ms]  
X_domain = 1H  
X_Freq = 391.78655441[MHz]  
X_offset = 5[ppm]  
X_points = 16384  
X_preamplifier = 1  
X_resolution = 0.44878791[Hz]  
X_sweep = 7.35294418[MHz]  
X_freq = 391.78655441[MHz]  
X_offset = 5[ppm]  
Tri_domain = 1H  
Rate = 391.78655441[MHz]  
Tri_offset = 5[ppm]  
Clipped = FALSE  
Nobs_return = 1  
Scans = 8  
Total_scans = 8  
X_90_width = 10.71[us]  
X_acq_time = 2.228224[ms]  
X_angle = 45[deg]  
X_atn = 1.9[GB]  
K_pulsa = 5.35[ns]  
X_gps = 0  
Tri_mode = 0  
Tri_preset = FALSE  
Initial_wait = 1[s]  
Nacquire = 30  
Relaxation_delay = 5[s]  
Repetition_time = 7.326224[ms]  
Temp_out = 21.1[°C]
----- PROCESSING PARAMETERS -----
dc_balance = 0 : FALSE
scout = 2.0[Ms] : 0.0[as]
trapenoid3 = 0[%] : 80[%] : 100[%]
zerofill = 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: UKI-361-carbon-1.jdf

Filename = UKI-361-carbon-3.jdf
Author = element
Experiment = single_pulse_Dec
Sample_id = 361
Solvent = CHLOROFORM-D
Creation_time = 15-SEP-2015 14:45:55
Revision_time = 12-SEP-2015 15:13:43
Comment = single pulse decoupled
Data_format = 1D COMPLEX
Dim_size = 2541
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = NMR 400
Spectrometer = JNM-ECS400

Field_strength = 9.20197068[TT] (390[MHz])
X_acq_duration = 1.06430644[s]
X_domain = 13C
X_freq = 98.51479726[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.03958051[Hz]
X_sweep = 30.76817724[MHz]

Trr_domain = 1H
Trr_freq = 391.7655441[MHz]
Trr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 200
Total_scans = 200

X_90_width = 8.8[us]
X_acq_time = 1.06430644[s]
Xangle = 30[deg]
X_atn = 4.9[dB]
X_pulse = 2.03333333[mus]
Trr_atn_dec = 22.526288[dB]
Trr_atn_noe = 22.526288[dB]
Trr_noise = WAVE
Decoupling = TRUE
Initial_wait = 1[s]
Moe = TRMS
Moe_time = 2[s]
Recvr_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.06430644[s]
Temp_gain = 20.4[dc]