SUPPORTING INFORMATION

for

Unexpected catalytic activity of a simple triethylborohydride in hydrosilylation of alkenes

Maciej Zaranek, Samanta Witomska, Violetta Patroniak and Piotr Pawluć

Faculty of Chemistry, Adam Mickiewicz University in Poznań Umultowska 89 B 61-614 Poznań, Poland

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Contact with authors:

- M. Zaranek m.zaranek@amu.edu.pl
- S. Witomska samanta.witomska@amu.edu.pl
- V. Patroniak violetta.patroniak@amu.edu.pl
- P. Pawluć piotr.pawluc@amu.edu.pl

1. Experimental procedures

1.1. General remarks

All reactions were performed in oven-dried glassware under argon atmosphere. Toluene was purified by MBraun SPS-8400 system and degassed after collection. Other solvents were dried by distillation over calcium hydride.

Gas chromatography was performed on a Bruker Scion 436-GC with a 30 m Agilent VF5-ms 0.53 mm Megabore column and a TCD detector. The temperature program was as follows: 60 °C (3 min), 20 °C/min, 280 °C (20 min). Decane was used as a reference. GC-MS analyses were performed on a Bruker Scion 436-GC with a 30 m Varian DB-5 0.25 mm capillary column and a Scion SQ-MS mass spectrometry detector. The temperature program was as follows: 60 °C (3 min), 10 °C/min, 250 °C (15 min). NMR analyses were performed on a Bruker Fourier 300 spectrometer.

1.2. General procedure of hydrosilylation catalysed by NaHBEt₃

1.0 mmol of silane, 2 mL of toluene, 2.0 mmol of alkene, and 0.1 mL of decane were placed in previously evacuated Schlenk bomb flask fitted with a plug valve. A reference sample was taken. Next, 0.1 mL of 1M solution of NaHBEt₃ (0.1 mmol) in toluene was added, reaction vessel was closed and heated at 100 °C with stirring.

After specified time, reaction mixture was cooled down to the room temperature and analysed using GC and GC-MS.

Products of hydrosilylation were isolated by first evaporating toluene on a rotary evaporator, then extraction with 1 mL of hexane followed by column chromatography of concentrated extract (SiO₂, hexane as eluent).

1.3. Yield determination of not isolated products

To determine selectivity, the peak area of desired product was divided by the sum of peak areas of all products obtained in the reaction. Chemical similarity, especially between isomeric products, is often high enough to assume essentially equal ionisation potentials, thus enabling direct comparison of the values. This was proven by cross-check of GC and GC-MS product ratios. So calculated selectivity multiplied by GC-determined conversion of silane is equal to GC-MS yield.

2. Analytical data of isolated products

2.1. Phenyl(1-phenylethyl)silane 3; colorless oil, yield: 190 mg (91%)



¹H NMR (300MHz, CDCl₃): δ 7.54-7.11 (m, 10H), 4.41 (d, 2H, *J*= 3.1 Hz), 2.69 (m, 1H), 1.54 (d, 3H, *J*= 7.5)

 ^{13}C NMR (75 MHz, CDCl_3): δ 144.61, 135.72, 131.45, 129.82, 128.44, 127.92, 127.19, 125.09, 25.45, 16.44

MS (70 *eV*): *m/z* (%):104 (100), 107 (60), 212 (47), 106 (25), 79 (24), 134 (21), 77 (20), 78 (11)

Conforms to the literature analytical data.¹

2.1. Diphenyl(1-phenylethyl)silane 5; colorless oil, yield: 256 mg (89%)



¹H NMR (300MHz, CDCl₃): δ 7.73-7.09 (m, 15H), 4.96 (d, 1H, J= 2.4Hz), 2.94 (qd, 1H, J= 3.3, 7.3 Hz), 1.58 (d, 3H, J= 7.4 Hz)

¹³C NMR (75 MHz, CDCl₃): δ 144.45, 135.84, 135.69, 133.14, 129.84 129.71, 128.30, 128.05, 127.84, 125.05, 27.09, 16.63

MS (70 eV): *m/z* (%):183 (100), 105 (20), 184 (16), 181 (16)

HRMS calcd for C₂₀H₂₀Si: 288.1334, found: 288.1337

2.2. Phenyl(2-phenylpropan-2-yl)silane 6; colorless oil, yield: 54 mg (24%)



¹*H NMR* (300*MHz*, *CDCI*₃): δ 7.44-7.30 (m, 6H), 7.26-7.12 (m, 4H), 4.31 (s, 2H), 1,48 (s, 6H)

 ^{13}C NMR (75 MHz, CDCl_3): δ 147.60, 136.00, 131.41, 129.75, 128.14, 127.69, 126.10, 124.87, 26.07, 25.21

MS (70 *eV*): *m/z* (%): 119 (100), 91 (70), 118 (51), 105 (21), 77 (17), 226 (16), 107 (14), 79 (14), 103 (12), 78 (11), 53 (10)

HRMS calcd for C₁₅H₁₈Si: 226.1178, found: 226.1182

2.3. Phenyl(1-(4-methylphenyl)ethyl)silane 7, colorless oil, yield: 103 mg (46%)



 ^{1}H NMR (300MHz, CDCl_3): δ 7.53-7.23 (m, 5H), 7.14-6.94 (m, 4H), 4.34 (s, 2H), 2.67-2.50 (m, 1H), 2.34 (s, 3H), 1.47 (d, 3H, J= 7.4 Hz)

 ^{13}C NMR (75 MHz, CDCl_3) δ 141.47, 135.67, 134.44, 131.62, 129.73, 129.12, 127.87, 127.02, 24.83, 20.99, 16.58

MS (70 eV): m/z (%):119 (100), 226 (31), 91 (22), 117 (17), 105 (14), 107 (12), 120 (12)

HRMS calcd for C₁₅H₁₈Si: 226.1178, found: 226.1184

2.4. (1-(2,4-dimethylphenyl)ethyl)(phenyl)silane 8; colorless oil, yield: 93 mg (39%)



^{*1}H NMR (300MHz, CDCl₃):* δ 7.52-7.31 (m, 5H), 7.09-6.95 (m, 3H), 4.37-4.27 (m, 2H), 2.84-2.70 (m, 1H), 2.32 (s, 3H), 2.23 (s, 3H), 1.47 (d, 3H, *J*= 7.4 Hz)</sup>

¹³C NMR (75 MHz, CDCl₃): 139.75, 135.60, 134.69, 134.18, 131.83, 131.04, 129.74, 127.89, 126.93, 126.00, 20.86, 20.32, 19.96, 16.74

MS (70 *eV*): *m/z* (%): 138 (100), 105 (23), 240 (18), 116 (13), 91 (12), 134 (11)

2.5. Triethoxy(1-phenylethyl)silane 9; colorless oil, yield: 195 mg (73%)



¹*H NMR (300MHz, CDCl*₃): δ 7.33-7.26 (m, 3H), 7.19-7.10 (m, 2H), 3.65 (q, 6H, *J*=7.0 Hz), 2.25 (q, 1H, *J*=7.6 Hz), 1.35 (d, 3H, *J*=7.6 Hz), 1.08 (t, 9H, *J*=7.0 Hz)

¹³C NMR (75 MHz, CDCl₃): δ 144.05, 128.04, 127.90, 124.81, 58.80, 26.15, 18.20, 15.58

MS (70 *eV*): *m/z* (%): 163 (100), 119 (58), 79 (30), 107 (17), 135 (16), 91 (14), 105 (11), 164 (10), 63 (10)

Conforms to the literature analytical data.²

2.6. 1,1-Diphenyl-1-(phenylsilyl)ethane **10**; colorless oil, yield: 187 mg (65%)



¹*H NMR* (300*MHz*, *CDCl*₃): δ 7.52-7.28 (m, 7H), 7.27-7.11 (m, 8H), 4.72 (s, 2H), 1.82 (s, 3H)

 ^{13}C NMR (75 MHz, CDCl_3): δ 147.33, 136.36, 130.95, 129.80, 128.28, 127.61, 125.57, 37.61, 25.53

MS (*70 eV*): *m/z* (%): 181 (100), 103 (37), 166 (30), 165 (28), 165 (24), 77 (19), 182 (18), 288 (14), 105 (11), 183 (10)

Conforms to the literature analytical data.1

2.7. (1,1-Diphenylethyl)diphenylsilane 11; white solid, yield: 331 mg (91%)



¹H NMR (300MHz, CDCl₃): δ 7.39-7.31 (m, 2H), 7.27-7.14 (m, 18H), 5.30 (s, 1H), 1.91 (s, 3H)

 ^{13}C NMR (75 MHz, CDCl_3): δ 146.87, 136.38, 133.16, 129.55, 128.82, 128.06, 127.61, 125.53, 39.25, 25.59

MS (70 *eV*): *m/z* (%): 183 (100), 105 (20), 181 (19), 184 (18), 103 (11)

HRMS calcd for C₂₆H₂₄Si: 364.1647, found: 364.1651

2.8. (1-(Naphthalen-2-yl)ethyl)(phenyl)silane12; colorless oil, yield: 218 mg (83%)



^{*1}H NMR (300MHz, CDCl₃):* δ 7.72-7.60 (m, 3H), 7.45-7.10 (m, 9H), 4.32-4.24 (m, 2H), 2.75-2.62 (m, 1H), 1.45 (d, 3H, *J* = 7.5 Hz)</sup>

^{*1*3}*C NMR* (*75 MHz, CDCl*₃): δ 142.29, 135.73, 133.83, 131.65, 131.33, 129.86, 127.94, 127.85, 127.63, 127.38, 126.75, 125.93, 124.90, 124.58, 25.72, 16.48

MS (70 eV): *m/z* (%): 155 (100), 262 (25), 153 (21), 156 (17), 128(10)

Conforms to the literature analytical data.³

2.9. (E)-phenyl(4-phenylbut-3-en-2-yl)silane13; colorless oil, yield: 195 mg (82%)



^{*i*}*H NMR (300MHz, CDCl*₃): δ 7.65-7.57 (m, 2H), 7.45-7.15 (m, 8H), 6.40-6.25 (m, 2H), 4.35-4.28 (m, 2H), 2.35-2.25 (m, 1H), 1.32 (d, 3H, J = 7.2 Hz)

¹³C NMR (75 MHz, CDCl₃): δ 138.03, 135.72, 133.06, 131.15, 129.85, 128.51, 128.00, 127.73, 126.61, 125.76, 22.91, 15.11

MS (*70 eV*): *m/z* (%): 131 (100), 196 (46), 91 (41), 107 (23), 105 (19), 129 (16), 115 (13), 132 (13), 130 (13), 116 (11), 238 (10)

Conforms to the literature analytical data.4

2.10. (E)-diphenyl(4-phenylbut-3-en-2-yl)silane 14; colorless oil, yield: 175 mg (56%)



¹*H NMR* (*300MHz*, *CDCl*₃): δ 7.65-7.60 (m, 4H), 7.50-7.30 (m, 10H), 7.23-7.16 (m, 1H), 6.42-6.22 (m, 2H), 4.83 (d, 2H, *J* = 2.8 Hz), 2.52 (qd, 1H, *J* = 2.7, 7.2 Hz), 1.33 (d, 3H, *J* = 7.2 Hz)

¹³C NMR (75 MHz, CDCl₃): δ 138.23, 135.69, 135.54, 133.02, 129.75, 128.46, 128.01, 127.94, 127.38, 126.49, 125.74, 24.73, 14.76

MS (70 eV): m/z (%): 183, (100), 105 (20), 184 (17), 181 (15), 272 (6), 91 (6)

HRMS calcd for C₂₂H₂₂Si: 314.1491, found: 314.1488

2.11. Dimethyl(phenyl)(1-(phenylsilyl)ethyl)silane 15; colorless oil, yield: 86 mg (32%)



^{*1}H NMR (300MHz, CDCl₃):* δ 7.47-7.38 (m, 4H), 7.31-7.19 (m, 6H), 4.30 (dd, 1H, *J*= 2.1, 5.8 Hz), 4.13 (t, 1H, *J*= 5.6 Hz), 1.06-0.94 (m, 3H), 0.43 (qdd, 1H, *J*= 2.4, 5.4, 7.6 Hz), 0.22 (s, 6H)</sup>

 ^{13}C NMR (75 MHz, CDCl_3): δ 136.89, 133.75, 132.15, 131.20, 127.78, 127.26, 126.24, 126.02, 9.11, 0.00, -4.61, -5.74

MS (*70 eV*): *m/z* (%): 135 (100), 192 (36), 105 (23), 177 (19), 121 (15), 107 (15), 136 (14), 133 (10)

2.12. (1-(Diphenylsilyl)ethyl)dimethyl(phenyl)silane 16; colorless wax, yield: 140 mg (41%)



¹*H NMR* (*300MHz, CDCl*₃): δ 7.45-7.10 (m, 15H), 4.69 (d, 1H, *J*= 3.6 Hz), 0.97-0.87 (m, 3H), 0.65 (ddq, 1H, *J*= 3.9, 7.8, 11.4 Hz), 0.01 (d, 6H, *J*= 3.2 Hz)

¹³C NMR (75 MHz, CDCl₃): δ 141.31, 137.89, 137.52, 137.46, 136.85, 136.11, 131.69, 131.67, 131.08, 130.19, 130.15, 129.91, 12.49, 5.34, -0.00, -1.66

MS (*70 eV*): *m/z* (%): 135 (100), 190 (71), 105 (50), 183 (35), 182 (29), 210 (28), 181 (24), 197 (23), 107 (18), 253 (17), 121 (16), 191 (15), 136 (13), 175 (12), 132 (11), 148 (11), 268 (11), 259 (10)

HRMS calcd for C₂₂H₂₆Si₂: 346.1573, found: 346.1568

2.13. Triphenyl(1-(phenylsilyl)ethyl)silane 17; colorless solid, yield: 347 mg (88%)



 ^{1}H NMR (300MHz, CDCl_3): δ 7.66-7.55 (m, 5H), 7.52-7.29 (m, 15H), 4.48 (d, 1H, J= 6.0 Hz), 4.30-4.15 (m, 1H), 1.35-1.25 (m, 4H)

 ^{13}C NMR (75 MHz, CDCl_3): δ 135.97, 135.38, 134.59, 132.76, 129.40, 127.92, 127.80, 11.91, - 0.90

MS (70 eV): *m/z* (%): 259 (100), 238 (31), 105 (27), 260 (25), 181 (20), 183 (10)

HRMS calcd for C₂₆H₂₆Si₂: 394.1573, found: 394.1570

2.14. (1-(Diphenylsilyl)ethyl)triphenylsilane 18; colorless solid, yield: 385 mg (82%)



¹*H* NMR (300MHz, CDCl₃): δ 7.59-7.50 (m, 8H), 7.46-7.19 (m, 17H), 5.03 (d, 1H, J= 2.0 Hz), 1.64 (qd, 1H, J= 2.2, 7.5 Hz), 1.34 (d, 3H, J= 7.5 Hz)

¹³C NMR (75 MHz, CDCl₃): δ 136.14, 135.88, 135.21, 135.08, 134.79, 133.70, 129.39, 129.30, 127.94, 127.74, 127.69, 11.5, 0.26

MS (70 *eV*): *m/z* (%): 259 (100), 314 (49), 181 (43), 105 (39), 210 (36), 260 (26), 182 (24), 183 (23), 315 (16), 155 (11), 180 (10), 392 (10)

HRMS calcd for $C_{32}H_{30}Si_2$: 470.1886, found: 470.1892

2.15. Tris(1-(glycidyloxy)propan-2-yl)(phenyl)silane **19**;colorless oil, yield: 421 mg (94%)

¹*H* NMR (300MHz, CDCl₃): δ 7.74 (d, 2H, J=6.5 Hz), 7.49-7.33 (m, 3H), 5.8 (ddd, 3H, J= 5.5, 10.7, 22.5 Hz), 5.21 (dd, 6H, J= 13.8, 30.1 Hz), 4.40-4.23 (m, 3H), 3.99 (d, 6H, J= 5.4 Hz), 3.52-3.43 (m, 3H), 3.34 (dd, 3H, J= 5.7, 9.6 Hz), 1.25 (d, 9H, J= 6.2 Hz)

 ^{13}C NMR (75 MHz, CDCl_3): δ 135.06, 135.00, 132.08, 130.08, 127.61, 116.59, 75.61, 72.11, 68.00, 20.61

MS (*70 eV*): *m/z* (%): 335 (100), 175 (62), 179 (45), 336 (24), 117 (22), 123 (20), 119 (20), 101 (18), 159 (18), 161 (18), 57 (17), 79 (15), 217 (15), 139 (13), 237 (12), 81 (12), 99 (12), 149 (11)

HRMS (ESI TOF) calcd for C₂₄H₃₈O₆SiNa: 473,2336, found: 473,2339

2.16. Bis(1-(glycidyloxy)propan-2-yl)(diphenyl)silane 20; colorless oil, yield: 358 mg (87%)



¹*H* NMR (300MHz, CDCl₃): δ 7.80-7.72 (m, 4H), 7.48-7.38 (m, 6H), 5.92 (ddd, 2H, J= 5.5, 10.7, 22.5 Hz), 5.24 (dd, 4H, J= 13.8, 27.1 Hz), 4.36-4.21 (m, 2H), 4.00 (dd, 4H, J= 1.1, 5.4 Hz), 3.54 (ddd, 2H, J= 2.1, 5.7, 9.6 Hz), 3.40 (dd, 2H, J= 5.6, 9.7 Hz), 1.28 (d, 6H, J= 6.2 Hz)

¹³C NMR (75 MHz, CDCl₃): δ 135.20, 135.01, 134.00, 133.80, 133.66, 130.10, 127.70, 116.67, 75.73, 72.14, 68.24, 20.75

MS (*70 eV*): *m/z* (%): 179 (100), 181 (18), 180 (17), 123 (17), 297 (15), 117 (15), 101 (15), 335 (13), 161 (11)

HRMS (ESI TOF) calcd for C₂₄H₃₂O₄SiK: 451,1707, found: 451,1712

2.17. (1-(glycidyloxy)propan-2-yl)(triphenyl)silane 21; colorless oil, yield: 165 mg (44%)



¹*H* NMR (300MHz, CDCl₃):57.79-7.69 (m, 6H), 7,53-7.38 (m, 9H), 5.86 (ddd, 1H, J=5.5, 10.7, 22.7 Hz), 5.31-5.13 (m, 2H), 4.31-4.16 (m, 1H), 3.96 (dd, 2H, J=6.0, 13.4), 3.53 (dd, 1H, J=6.0, 9.7 Hz), 3.42 (dd, 1H, J=5.3, 9.7 Hz), 1,27 (d, 3H, J=6.2 Hz)

¹³C NMR (75 MHz, CDCl₃): δ 135.61, 134.89, 129.95, 127.82, 116.70, 75.90, 72.12, 68.84, 20.78

MS (70 eV): *m/z* (%): 259 (100), 179 (60), 297 (35), 181 (31), 260 (24), 199 (19), 180 (16), 105 (11)

HRMS (ESI TOF) calcd for C₂₄H₂₆O₂SiNa: 397,1600, found: 397,1606

2.18. (1-(Glycidyloxy)propan-2-yl)(dimethyl)phenylsilane 22; colorless oil



¹*H* NMR (300MHz, CDCl₃):δ7.67-7.57 (m, 2H), 7.43-7.34 (m, 3H), 5.88 (ddt, 1H, J=5.5, 10.7, 17.1 Hz), 5.26 (ddd, 1H, J=1.6, 3.3, 17.3 Hz), 5.17 (dd, 1H, J=1.6, 10.4 Hz), 4.10-3.90 (m, 3H), 3.33 (qd, 2H, J=5.7, 9.7 Hz), 1.15 (d, 3H, J=6.3 Hz), 0.41 (s, 6H)

¹³C NMR (75 MHz, CDCl₃): δ 138.43, 134.90, 133.55, 129.47, 127.74, 116.65, 75.87, 72.15, 67.96, 20.71, 1.02, 1.13

MS (70 *eV*): *m/z* (%): 135 (100), 75 (72), 117 (54), 179 (27), 173 (26), 105 (15), 77 (14), 136 (13), 131 (12), 91 (10), 99 (10)

HRMS (ESI TOF) calcd for C₁₄H₂₂O₂SiK: 273,1287, found: 273,1289

2.19 (2-(allyloxy)ethoxy)triphenylsilane – identified product of a reaction of triphenylsilane with O-THP 2-allyloxyethanol



¹*H* NMR (300MHz, CDCl₃):δ7.78-7.60 (m, 6H), 7.50-7.7.30 (m, 9H), 5.87 (ddd, 1H, J=5.3, 10.4, 16.2 Hz), 5.24 (d, 1H, J=17.2 Hz), 5.15 (d, 1H, J=10.4 Hz), 3.98 (d, 2H, J=5.9 Hz), 3.94 (d, 2H, J=5.4 Hz), 3.60 (t, 2H, J=5.3 Hz)

2.20 tert-butoxydiphenylsilane; colorless oil



¹H NMR (300MHz, CDCl₃): 7.67-7.55 (m, 4H), 7.42-7.30 (m, 6H), 5.55 (s, 1H, J=12.63 Hz), 1.33 (s, 9H)

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4. GC-MS chromatogram of a reaction of 1,1,2,2-tetramethyldisiloxane with styrene and NaHBEt₃

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MS Data Review Active Chromatogram and Spectrum Plots - 2016-09-06 14:45