other ions. Further study is currently under way.

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Generation and Reactivity of Tolylsilylenes

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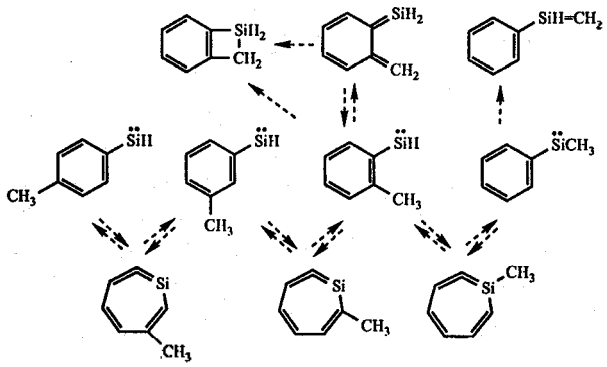
The isomeric tolylmethylenes have been studied in considerable detail over the past two decades.[1~3] Much of the impetus for these works came from mechanistic studies of the interconversion to give the benzocyclobutene and styrene. However, tolylsilylenes, analogues of tolylmethylenes have apparently not been reported. In this context, we thought it might be of some interest to study the reactivities of the *o*-, *m*-, and *p*-tolylsilylenes in comparison with those observed on chemistry of isomeric tolylmethylenes (Scheme 1).[2,3]

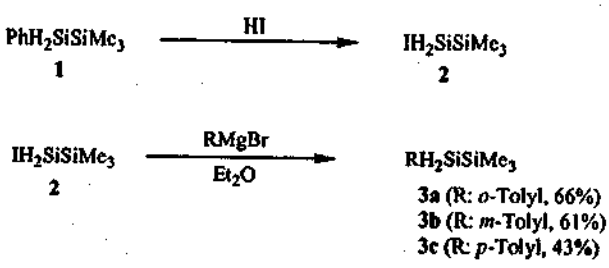
The following synthetic scheme, including the acid-cleavage of 2-phenyldisilane with HI,[4] was adopted to obtain the required tolylsilylene precursors.

Flow vacuum pyrolyses (FVP) of **3a-c**[5] at 600 ℃ in the presence of a 30-fold excess of 2,3-dimethylbutadiene as the trapping agent gave 1-silacyclopent-3-ene derived from the addition of tolylsilylenes to the diene in 52, 24, and 48% yields, respectively.[6] When the precursors **3a-c** were pyrolyzed in the absence of trapping agent, benzosilacyclobutene (**12a**)[7] *via* the intramolecular γ C-H insertion of *o*-tolylsilylene was obtained in 70% yield, but in case of *m*- and *p*-tolylsilylenes, the formation of benzosilacyclobutene due to the interconversion *via* methylsilacycloheptatetraene intermediate shown in Scheme 1 was not observed. In the presence of triethylsilane as a trapping agent, the pyrolysis of **3b-c** gave 1,1,1-triethyl-2-(*m*-tolyl)disilane, **5b** and 1,1,1-triethyl-2-(*p*-tolyl)disilane, **5c** in 40% and 37% yields, respectively.[8] Interestingly, the pyrolysis of **3a** gave 1,2-benzo-3-sila-1-cyclobutene, **12a** and no **5a** was observed. This result strongly suggested that an intramolecular C-H insertion reaction of *o*-tolylsilylene was much favor over an intermolecular Si-H insertion.

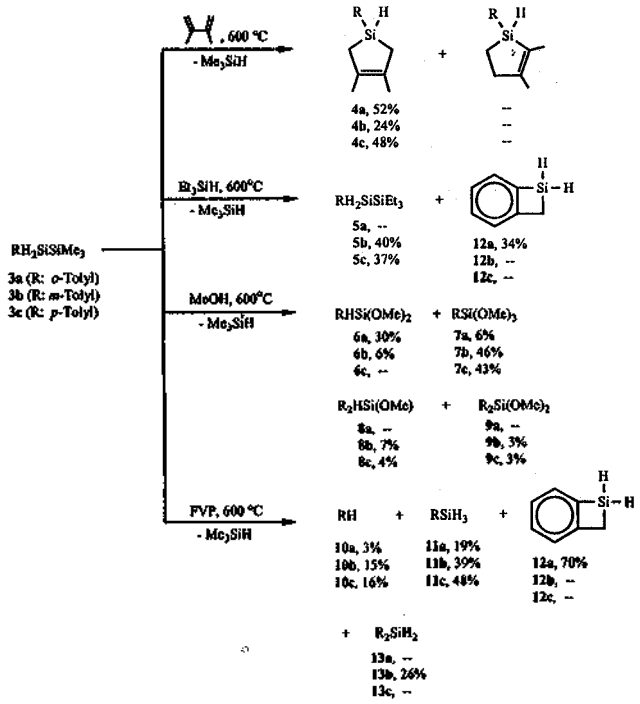
It was also interesting to note that tolylsilanes, **11a-c**[7] were obtained in 19, 39 and 48% yields, respectively, which were presumably formed due to the intramolecular β C-H insertion.



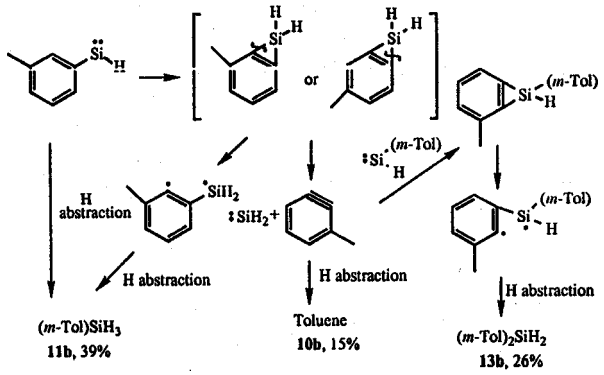
Scheme 1. The Possible Isomerization of Tolylsilylenes.



Scheme 2.



Scheme 3. The Results of FVP of 2-Tolyldisilanes.



Scheme 4. Reaction Mechanism of (*m*-Tolyl) Silylene.

In order to test the possible mechanism for the formation of tolylsilanes the FVP of **3a-c**[6] were conducted at 600 ℃ in the presence of an excess of MeOH, which gave the results consistent with the mechanism proposed in Scheme 4.[9,10]

In conclusion, the free *o*-, *m*- and *p*-tolylsilylenes were thermally generated. No evidence for the products suggesting that *m*- and *p*-tolylsilylenes rearrange by a ring expansion to the silacycloheptatrienylidene or silacycloheptatetraene could be found, but $RSiH_3$ and R_2SiH_2 (R : *o*-tolyl, *m*-tolyl, *p*-tolyl) formed through the intramolecular β C-H insertion were obtained in high yields.

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5. 1,1,1-Trimethyl-2-(*o*-tolyl)disilane (**3a**): ^{1}H NMR ($CDCl_3$, 500 MHz): 0.00 ppm (s, $SiMe_3$, 9H), 2.19 ppm (s, $C_6H_4\underline{Me}$, 3H), 4.22 ppm (s, SiH_2, 2H), 6.89-7.44 ppm (m, $C_6\underline{H}_4Me$, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): −0.18 ppm, 24.15 ppm, 126.27 ppm, 128.99 ppm, 130.37 ppm, 130.53 ppm, 137.92 ppm, 144.65 ppm. IR (cm^{-1}): 3050 (s), 2940 (vs), 2311 (vs), 1586 (s), 1377 (s), 1280 (w), 1244 (vs), 1125 (s), 622 (vs). Mass (m/z, relative intensity): 194 (21, M^+), 149 (28), 135 (5), 120 (18), 93 (10), 73 (100). HR Mass: calculated 194.0947, found 194.0923.
1,1,1-Trimethyl-2-(*m*-tolyl)disilane (**3b**): ^{1}H NMR ($CDCl_3$, 500 MHz): 0.00 ppm (s, $SiMe_3$, 9H), 1.98 ppm (s, $C_6H_4\underline{Me}$, 3H), 4.25 ppm (s, SiH_2, 2H), 6.83-7.23 ppm (m, $C_6\underline{H}_4Me$, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): 0.00 ppm, 22.5 ppm, 128.90 ppm, 131.27 ppm, 132.25 ppm, 134.24 ppm, 137.90 ppm, 138.56 ppm. IR (cm^{-1}): 3071 (w), 2939 (s), 2100 (vs), 1618 (w), 1243 (s), 1114 (s), 916 (vs), 861 (w), 732 (s). Mass (m/z, relative intensity): 194 (12, M^+), 179 (6), 149 (22), 120 (14), 119 (13), 93 (7), 73 (100), 43 (5). HR Mass: calculated 194.0947, found 194.0937.
1,1,1-Trimethyl-2-(*p*-tolyl)disilane (**3c**): ^{1}H NMR (C_6D_6, 500 MHz): 0.14 ppm (s, $SiMe_3$, 9H), 2.09 ppm (s, $C_6H_4\underline{Me}$, 3H), 4.39 ppm (s, SiH_2, 2H), 6.99-7.48 ppm (m, $C_6\underline{H}_4Me$, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): −1.22 ppm, 21.35 ppm, 127.41 ppm, 129.39 ppm, 136.16 ppm, 138.88 ppm. IR (cm^{-1}): 3057 (s), 2907 (s), 2289 (vs), 1902 (w), 1597 (s), 1497 (s), 1389 (s), 1257 (vs), 1187 (w). Mass (m/z, relative intensity): 194 (10, M^+), 179 (5), 149 (17), 119 (17), 105 (7), 93 (12), 73 (100), 43 (11). HR Mass: calculated 194.0947, found 194.0965.
6. 3,4-Dimethyl-1-(*o*-tolyl)-1-silacyclopet-3-ene (**4a**): ^{1}H NMR ($CDCl_3$, 500 MHz): 1.50 ppm (d, ^3J=19.5 Hz, $Si\underline{CH}_2$, 2H), 1.56 ppm (s, $C{=}C\underline{CH}_3$, 6H), 1.60 ppm (d, ^3J=18.8 Hz, $SiCH_2$, 2H), 2.18 ppm (s, $C_6H_4\underline{Me}$, 3H), 4.76 ppm (q, ^3J= 3.5 Hz, SiH, 1H), 6.91-7.44 ppm (m, $C_6\underline{H}_4Me$, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): 19.89 ppm, 23.02 ppm, 23.14 ppm, 126.14 ppm, 130.40 ppm, 130.86 ppm, 131.56 ppm, 136.21 ppm, 144.85 ppm. Mass (m/z, relative intensity): 202 (78, M^+), 131 (29), 119 (44), 110 (100), 95 (35).
3,4-Dimethyl-1-(*m*-tolyl)-1-silacyclopent-3-ene (**4b**): ^{1}H NMR ($CDCl_3$, 500 MHz): 1.69 ppm (d, ^3J=17 Hz, $SiCH_2$, 2H), 1.84 ppm (s, $C{=}C\underline{CH}_3$, 6H), 1.85 ppm (d, ^3J=15.7 Hz, $SiCH_2$, 2H), 2.42 ppm (s, $C_6H_4\underline{Me}$, 3H), 4.69 ppm (q, ^3J=15 Hz, SiH, 1H), 7.25-7.46 ppm (m, $C_6\underline{H}_4Me$, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): 19.33 ppm, 21.62 ppm, 22.80 ppm, 128.07 ppm, 130.50 ppm, 130.97 ppm, 131.65 ppm, 135.28 ppm, 135.84 ppm, 137.48 ppm. Mass (m/z, relative intensity): 202 (70, M^+), 173 (2), 159 (13), 121 (7), 110 (100), 95 (36), 67 (8), 53 (8).
3,4-Dimethyl-1-(*p*-tolyl)-1-silacyclopent-3-ene (**4c**): ^{1}H NMR ($CDCl_3$, 500 MHz): 1.73 ppm (d, ^3J=16.5 Hz, $Si\underline{CH}_2$, 2H), 1.89 ppm (s, $C{=}C\underline{CH}_3$, 6H), 1.91 ppm (d, ^3J=16.7 Hz, $Si\underline{CH}_2$, 2H), 2.47 ppm (s, $C_6H_4\underline{Me}$, 3H), 4.76 ppm

(q, ^3J=3.2 Hz, SiH, 1H), 7.27-7.61 ppm (m, $C_6\underline{H_4}Me$, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): 19.37 ppm, 21.71 ppm, 22.93 ppm, 23.14 ppm, 129.00 ppm, 130.99 ppm, 132.34 ppm, 134.71 ppm, 139.62 ppm. Mass (m/z, relative intensity): 202 (56, M^+), 187 (11), 159 (13), 121 (10), 110 (100), 95 (36), 67 (16).

7. (*o*-Tolyl)silane (**11a**): ^1H NMR (C_6D_6, 500 MHz): 2.20 ppm (s, $C_6H_4\underline{Me}$, 3H), 4.24 ppm (s, SiH_3, 3H), 6.93-7.46 ppm (m, $C_6\underline{H_4}Me$, 4H). Mass (m/z, relative intensity): 122 (63, M^+), 119 (22), 105 (26), 91 (100), 77 (6), 67 (9), 53 (12).
(*m*-Tolyl)silane (**11b**): ^1H NMR (C_6D_6, 500 MHz): 2.37 ppm (s, $C_6H_4\underline{Me}$, 3H), 4.20 ppm (s, SiH_3, 3H), 7.23-7.43 ppm (m, $C_6\underline{H_4}Me$, 4H). Mass (m/z, relative intensity): 122 (78, M^+), 105 (23), 93 (19), 91 (100), 67 (7), 53 (9), 42 (5).
(*p*-Tolyl)silane (**11c**): ^1H NMR (C_6D_6, 500 MHz): 2.39 ppm (s, $C_6H_4\underline{Me}$, 3H), 4.22 ppm (s, SiH_3, 3H), 7.22 ppm (d, ^3J=7.8 Hz, $C_6\underline{H_4}Me$, 2H), 7.52 ppm (d, ^3J=7.7 Hz, $C_6\underline{H_4}Me$, 2H). Mass (m/z, relative intensity): 122 (54, M^+), 105 (20), 91 (100), 90 (8), 67 (9), 65 (19), 53 (20), 39 (12).
1,2-Benzo-3-sila-1-cyclobutene (**12a**): ^1H NMR (C_6D_6, 80 MHz): 2.23 ppm (t, ^3J=4 Hz, CH_2, 2H), 4.63 ppm (t, ^3J=4.8 Hz, SiH_2, 2H), 6.69-7.07 ppm (m, C_6H_4, 4H). Mass (m/z, relative intensity): 120 (100, M^+), 106 (3), 105 (80), 93 (29), 79 (4), 77 (7), 66 (11), 53 (16).
Bis(*m*-tolyl)silane (**13b**): ^1H NMR (C_6D_6, 500 MHz): 2.05 ppm (s, $C_6H_4\underline{Me}$, 3H), 5.16 ppm (s, SiH_2, 2H), 7.00-7.44 ppm (m, $C_6\underline{H_4}Me$, 4H). Mass (m/z, relative intensity): 212 (40, M^+), 195 (3), 134 (5), 120 (100), 104 (53), 93 (16), 912 (12), 67 (4), 53 (6).

8. 1,1,1-Triethyl-2-(*m*-tolyl)disilane (**5b**): ^1H NMR (C_6D_6, 500 MHz): 0.68 ppm (q, ^3J=7.9 Hz, $SiCH_2\underline{CH_3}$, 6H), 0.98 ppm (t, ^3J=7.8 Hz, $SiCH_2\underline{CH_3}$, 9H), 2.11 ppm (s, $C_6H_4\underline{Me}$, 3H), 4.45 ppm (s, SiH_2, 2H), 6.98-7.46 ppm (m, $C_6\underline{H_4}Me$, 4H). Mass (m/z, relative intensity): 236 (17, M^+), 207 (4), 179 (9), 151 (22), 115 (100), 87 (85), 59 (18), 43 (3).
1,1,1-Triethyl-2-(*p*-tolyl)disilane (**5c**): ^1H NMR (C_6D_6, 500 MHz): 0.67 ppm (q, ^3J=7.9 Hz, $SiCH_2CH_3$, 6H), 0.98 ppm (t, ^3J=8.0 Hz, $SiCH_2\underline{CH_3}$, 9H), 2.08 ppm (s, $C_6H_4\underline{Me}$, 3H), 4.46 ppm (s, SiH_2, 2H), 7.00-7.53 ppm (m, $C_6\underline{H_4}Me$, 4H). Mass (m/z, relative intensity): 236 (20, M^+), 207 (4), 179 (10), 151 (24), 115 (100), 87 (90), 59 (22), 53 (4).

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10. Dimethoxy(*o*-tolyl)silane (**6a**): ^1H NMR (C_6D_6, 500 MHz): 2.47 ppm (s, $C_6H_4C\underline{H_3}$, 3H), 3.40 ppm (s, SiOMe, 6H), 5.17 ppm (s, SiH, 1H), 6.97-7.79 ppm (m, $C_6\underline{H_4}CH_3$, 4H). Mass (m/z, relative intensity): 182 (14, M^+), 152 (2), 151 (5), 119 (4), 105 (4), 91 (100), 77 (3), 61 (41).
Dimethoxy(*m*-tolyl)silane (**6b**): Mass (m/z, relative intensity): 182 (52, M^+), 181 (64), 151 (22), 133 (2), 121 (10), 91 (100), 77 (3), 59 (39), 45 (4).
Trimethoxy(*o*-tolyl)silane (**7a**): Mass (m/z, relative intensity): 212 (15, M^+), 180 (8), 165 (4), 150 (7), 121 (100), 92 (11), 91 (99), 59 (30).
Trimethoxy(*m*-tolyl)silane (**7b**): Mass (m/z, relative intensity): 212 (33, M^+), 181 (20), 167 (3), 151 (8), 120 (100), 91 (58), 59 (20), 45 (3).
Trimethoxy(*p*-tolyl)silane (**7c**): Mass (m/z, relative intensity): 212 (24, M^+), 181 (14), 151 (8), 123 (3), 120 (100), 90 (59), 59 (20), 45 (3).
Methoxybis(*m*-tolyl)silane (**8b**): Mass (m/z, relative intensity): 242 (10, M^+), 211 (6), 179 (2), 150 (100), 119 (12), 105 (21), 65 (5), 59 (45).
Methoxybis(*p*-tolyl)silane (**8c**): Mass (m/z, relative intensity): 242 (14, M^+), 211 (14), 179 (2), 150 (100), 119 (10), 105 (5), 91 (8), 59 (18).
Dimethoxybis(*m*-tolyl)silane (**9b**): Mass (m/z, relative intensity): 272 (20, M^+), 241 (4), 183 (10), 181 (100), 151 (27), 105 (36), 91 (13), 59 (22).
Dimethoxybis(*p*-tolyl)silane (**9c**): Mass (m/z, relative intensity): 272 (22, M^+), 241 (4), 211 (4), 181 (100), 151 (23), 121 (23), 91 (9), 59 (14).

Unusual Effect of the Connecting Tether Direction of a Liquid Chromatographic Chiral Stationary Phase on the Chiral Recognition

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Subtle structural changes of Pirkle-type chiral stationary phases (CSPs) for the liquid chromatographic resolution of enantiomers have been known to show often remarkable influences on enantioselectivity. For example, increasing the π-basicity of the aryl functionality of π-basic Pirkle-type CSPs or changing the conformational rigidity of CSPs has affected their enantioselectivities.[1] The manner of connecting a chiral selector to solid column support has been another important factor influencing the degree of enantioselectivity.[2] Especially, the direction and the length of the connecting tether of Pirkle-type CSPs have been engineered to manipulate the resolution trends for resolving a homologous series of racemic analytes in elucidating the chiral recognition mechanism or to enhance the enantioselectivity.[3]

In this study, we prepared a new CSP (**1**) by bonding N-(3,5-dinitrobenzoyl)-(R)-4-hydroxyphenylglycine to silica gel through the 4-hydroxy functionality.[4] CSP **1** maintains the integrity of the structure of a representative commercial π-acidic CSP (**2**) derived from N-(3,5-dinitrobenzoyl)-(R)-phenylglycine except the direction of the connecting tether. To elucidate the characteristics of CSP **1**, we resolved various racemic α-amino acid derivatives on CSP **1** and compared the resolution results with those on CSP **2**. We consequently found there are drastic discrepancies between the chromatographic resolving ability of CSP **1** and **2** for the two enantio-