

Supporting Information

A Facile Synthesis of 1,1-bis(silyl)ethenes

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Experimental

Compound 1

A 50 mL (0.359mol) of dry triethylamine in 200mL dry pentane was introduced into a flame-dried three-necked, 500mL round-bottomed flask equipped with a magnetic stirring bar, rubber septum cap and argon bubbling tube. To the resulting solution 9.1mL (0.161mol) of ethylene glycol was added. 45.3mL (0.330mol) of chlorodimethylvinylsilane was subsequently added over 1h and the reaction mixture was stirred under the flow of argon for 2h at room temperature. After the substrate disappearance was confirmed by GC, the resulting salt was filtered off and the volatiles were removed in evaporator. Distillation under reduced pressure (42-44 °C/0.5mmHg) afforded 33.39g of compound **1** in 90% yield as a colorless liquid. ¹H NMR (CDCl₃) δ (ppm): 0.22 (s, 12H), 3.88 (s, 4H), 5.86-5.94 (dd, J=19, 5 Hz, 2H), 5.99-6.18 (dd, J=5, 14 Hz, 2H), 6.22-6.58 (dd, J=14, 19 Hz, 2H), ¹³C NMR (CDCl₃) δ (ppm): 1.2, 64.4, 128.6, 138.5. Anal. calc. for C₁₀H₂₂O₂Si₂: C, 52.12; H, 9.62; Found: C, 51.96; H, 9.80.

Compound 2

0.828g [RuHCl(CO)(PPh₃)₃] (8.7x10⁻⁴mol) and 20.0g (0.087mol) of compound **1** were placed in the two-necked, 50mL flask equipped with a magnetic stirring bar and a reflux condenser. The reaction mixture was heated for 1h at 80°C with stirring. The cyclic product was isolated by “bulb to bulb” distillation to give 14.93g of compound **2** in 85% yield as a colorless liquid. ¹H NMR (CDCl₃) δ (ppm): 0.25 (s, 12H), 3.65 (s, 4H), 6.20 (s, 2H), ¹³C NMR (CDCl₃) δ (ppm): -1.5, 66.6, 139.7, 157.7, Anal. calc. for C₈H₁₈O₂Si₂: C, 47.47; H, 8.96; Found: C, 47.51; H, 9.14.

Compound (I)

A solution of 2.0g (0.01mol) of compound **2** in 20mL dry THF was introduced into flame-dried, two-necked, 100mL round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, rubber septum cap and argon bubbling tube. Then a 0.025 mol amount of methylmagnesium iodide in dry THF was added dropwise. The reaction mixture was refluxed under argon for 24h. The excess amount of Grignard reagent was quenched by adding MeOH/diethyl ether solution and the mixture was extracted from ether/H₂O. The ethereal phase was dried over MgSO₄ and filtered, the volatiles removed in evaporator and the mixture was passed through a silica gel column (eluent-hexane). After isolation by distillation under argon (bp. 133°C/760mmHg) 1.29g of compound **I** was afforded in 76% yield as colorless

liquid. ^1H NMR (CDCl_3) δ (ppm): 0.10 (s, 18H), 6.29 (s, 2H). ^{13}C NMR (CDCl_3) δ (ppm): –0.3, 139.7, 154.7. Anal. calc. for $\text{C}_8\text{H}_{20}\text{Si}_2$: C, 55.73; H, 11.69; Found: C, 56.16; H, 12.33.

Compound (II)

This compound was synthesized in the same method as the synthesis of compound **I**, but the reaction mixture had to be heated for 48h. Compound **II** was obtained in 73% yield (1.44g) as a colorless liquid (bp. $173^\circ\text{C}/760\text{mmHg}$). ^1H NMR (CDCl_3) δ (ppm): 0.07 (s, 12H), 0.53-0.58 (q, 4H), 0.88-0.93 (t, 6H), 6.31 (s, 2H). ^{13}C NMR (CDCl_3) δ (ppm): –2.7, 7.4, 7.7, 140.9, 152.3. Anal. calc. for $\text{C}_{10}\text{H}_{24}\text{Si}_2$: C, 59.91; H, 12.07; Found: C, 59.58; H, 12.30.

Compound (III)

This compound was synthesized by analogous reaction with phenylmagnesium bromide and isolated by a procedure similar to that mentioned above. Distillation under reduced pressure ($110\text{-}113^\circ\text{C}/0.5\text{mmHg}$) afforded 2.56g of compound **III** in 88% yield as a colorless oil. ^1H NMR (CDCl_3) δ (ppm): 0.47 (s, 12H), 6.63 (s, 2H), 7.48-7.63 (m, 10H). ^{13}C NMR (CDCl_3) δ (ppm): –1.8, 143.8, 150.8, 128.7-138.7. Anal. calc. for $\text{C}_{18}\text{H}_{24}\text{Si}_2$: C, 72.90; H, 8.16; Found: C, 72.35; H, 8.13.

Compound (IV)

This compound was synthesized in essentially the same manner as **I** by the reaction between 2,2,4,4-tetramethyl-1,5-dioxo-2,4-disila-3-*exo*-methylenecycloheptane and vinylmagnesium bromide. Compound **IV** was obtained in 62% yield (1.20g) as a colorless liquid (bp. $168^\circ\text{C}/760\text{mmHg}$). ^1H NMR (CDCl_3) δ (ppm): 0.19 (s, 12H), 5.65-5.73 (dd, $J=4$, 20 Hz, 2H), 5.96-6.02 (dd, $J=4$, 14 Hz, 2H), 6.14-6.26 (dd, $J=14$, 20 Hz, 2H), 6.38 (s, 2H). ^{13}C NMR (CDCl_3) δ (ppm): -2.2, 131.8, 139.2, 142.3, 151.1. Anal. calc. for $\text{C}_{10}\text{H}_{20}\text{Si}_2$: C, 61.14; H, 10.24; Found: C, 60.23; H, 10.62.

Compound (V)

A solution of 2.0g (0.01mol) compound **2** in 20mL dry diethyl ether was introduced into flame-dried, two-necked, 100mL round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, rubber septum cap and argon bubbling tube. Then a 0.03 mol amount of allylmagnesium bromide in dry diethyl ether was added dropwise. The reaction mixture was refluxed under argon for 48h. The excess amount of Grignard reagent was quenched by adding $\text{MeOH}/\text{Et}_2\text{O}$ solution. The suspended salt was filtered off and the volatiles were evaporated in vacuo. After isolation by distillation under reduced pressure ($58^\circ\text{C}/0.5\text{mmHg}$) 1.51g of compound **V** was afforded in 68% yield as a colorless liquid. ^1H NMR (CDCl_3) δ (ppm): 0.12 (s, 12H), 1.60 (d, 4H), 4.82-4.83 (m, $J=14$, 5 Hz, 2H), 4.85-4.88 (m, $J=17$, 5 Hz,

2H), 5.67-5.82 (m, J=9, 17 Hz, 2H), 6.35 (s, 2H). ^{13}C NMR (CDCl_3) δ (ppm): -2.6, 24.0, 113.1, 134.8, 141.9, 151.1. Anal. calc. for $\text{C}_{12}\text{H}_{24}\text{Si}_2$: C, 64.20; H, 10.78; Found: C, 64.63; H, 10.52.

Compound (VI)

A solution of 2.0g (0.01mol) of compound **2** in 20mL dry THF was introduced into flame-dried, two-necked, 100mL round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, rubber septum cap and argon bubbling tube. Then a 0.03 mol amount of 3-butenylmagnesium bromide in dry THF was added dropwise. The reaction mixture was refluxed under argon for 72h. The excess amount of Grignard reagent was quenched by adding MeOH/THF solution. The suspended salt was filtered off and the volatiles were evaporated in vacuo. The obtained mixture was injected into a silica gel column (eluent-hexane) and compound **VI** was isolated by reduced pressure distillation (60 °C/0.5mmHg) in 55% yield (1.37g) as a colorless liquid. ^1H NMR (CDCl_3) δ (ppm): 0.11 (s, 12H), 0.65-0.77 (t, 4H), 2.00-2.06 (m, 4H), 4.91-4.87 (m, J=10, 5 Hz, 2H), 4.95-5.02 (m, J=17, 5 Hz, 2H), 5.82-5.95 (m, J=10, 16 Hz, 2H), 6.33 (s, 2H). ^{13}C NMR (CDCl_3) δ (ppm): -1.9, 15.3, 28.1, 112.6, 141.3, 141.6, 151.9. Anal. calc. for $\text{C}_{14}\text{H}_{28}\text{Si}_2$: C, 66.58; H, 11.18; Found: C, 64.56; H, 11.30.

Compound 3

3.0g of compound **2** (0.015mol) in 10mL of THF were placed in the two-necked, 50mL flask equipped with a magnetic stirring bar and a reflux condenser. Then 0.29mL (0.016mol) of water and several drops of aqueous solution of HCl were added. The reaction mixture was refluxed for 4h with stirring. The solvent was evaporated in vacuo and the cyclic product was isolated by distillation under reduced pressure (68 °C/0.5mmHg) to give 2.06g of **4** in 88% yield.

^1H NMR (CDCl_3) δ (ppm): 0.28 (s, 24H), 6.19 (s, 4H). ^{13}C NMR (CDCl_3) δ (ppm): 1.1, 139.9, 156.6. Anal. calc. for $\text{C}_{12}\text{H}_{28}\text{O}_2\text{Si}_4$: C, 45.60; H, 8.86; Found: C, 45.56; H, 8.81.