Silicon–Carbon Unsaturated Compounds. 36. Chemical Behavior of 1,2,2,2-Tetramethylphenylvinyldisilane in the Presence of a Nickel(0) Catalyst

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Summary: The reaction of 1,2,2,2-tetramethylphenylvinyldisilane (**1**) with dimethylphenylvinylsilane in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) at 220 °C in mesitylene gave (*E*)-1-{[2-(dimethylphenylsilyl)ethyl]methylphenylsilyl}-2-(trimethylsilyl)ethene and a dimer of **1** in 55 and 36% yields. Similar treatment of **1** with 2,3-dimethylbutadiene at 150 °C afforded (*Z*)-2,3-dimethyl-1-(methylphenylvinylsilyl)-4-(trimethylsilyl)but-2-ene, while with 1,3-cyclohexadiene at 180 °C, **1** produced a 1:1 mixture of *cis*- and *trans*-1-(methylphenylvinylsilyl)-4-(trimethylsilyl)-2-cyclohexene.

We have found that treatment of vinyldisilanes with a catalytic amount of tetrakis(triethylphosphine)nickel(0) in a sealed glass tube at 220 °C leads to dimerization products which can best be explained by the formation of a silene intermediate.[1] In order to learn more about the reactive intermediate involved in this system, we investigated the nickel-catalyzed reaction of 1,2,2,2-tetramethylphenylvinyldisilane (1) in the presence of a trapping agent.

First, we carried out the dimerization reaction of 1 with the use of a solvent in the presence of a catalytic amount of freshly prepared tetrakis(triethylphosphine)nickel(0).[2] Interestingly, the use of mesitylene as the solvent resulted in the formation of the dimer in higher yield than that in the absence of the solvent. Thus, heating a solution of 1 in the presence of the nickel catalyst in mesitylene in a degassed sealed tube at 220 °C for 24 h gave a dimer, (*E*)-1-{[2-(1,2,2,2-tetramethyl-1-phenyldisilanyl)ethyl]-methylphenylsilyl}-2-(trimethylsilyl)ethene (2) in 77% yield. All spectral data obtained for the product 2 were identical with those of the authentic sample reported previously.[1]

We carried out the reaction of 1 in the presence of dimethylphenylvinylsilane as a trapping agent under the same conditions. In this reaction, (*E*)-1-{[2-(dimethylphenylsilyl)ethyl]methylphenylsilyl}-2-(trimethylsilyl)ethene (3) was obtained in 55% yield, in addition to a 36% yield of the dimer 2. No other isomers of 3 were detected by either spectrometric analysis or GLC analysis.

The ^{1}H NMR spectrum of 3 reveals three resonances at δ 0.06, 0.24, and 0.30 ppm, attributed to trimethylsilyl, dimethylsilyl, and methylsilyl protons, respectively, and also shows multiplet resonances at 0.69–0.71 ppm and two doublets at 6.54 (J = 23 Hz) and 6.79 (J = 23 Hz) ppm, due to ethylene protons and olefin protons, as well as phenyl ring protons at 7.30–7.55 ppm. The coupling constant of the olefin protons clearly indicates that compound 3 must have the *E* configuration.

We have examined the nickel-catalyzed reaction of 1 with conjugated dienes. The reaction of 1 with a small excess of 2,3-dimethylbutadiene in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) in mesitylene in a sealed degassed tube at 220 °C for 24 h gave a double-silylated product, (*Z*)-2,3-dimethyl-1-(methylphenylvinylsilyl)-4-(trimethylsilyl)but-2-ene (6) in 92% yield. The product 6 can also be produced under much milder conditions. Thus, the reaction of 1 with 2,3-dimethylbutadiene in the presence of the nickel catalyst at 150 °C for 24 h afforded the product 6 in almost quantitative yield. In the absence of 2,3-dimethylbutadiene under the same conditions, compound 1 afforded no dimerization product 2, but the starting compound 1 was recovered unchanged.

The *Z* configuration of the product 6 was confirmed by NOE-FID difference experiments at 270 MHz. Thus, saturation of the methylene protons (δ 1.37 ppm) bound to a trimethylsilyl group produced a positive NOE of the methylene protons attached to a methylphenylvinylsilyl group and methyl protons at the C-3 position. Similar irradiation of the methylene protons (δ 1.77 ppm) attached to the methylphenylvinylsilyl group led to the strong enhancement of the methylene protons having the trimethylsilyl group and also of the methyl protons at the C-2 position, as well as methyl and phenyl protons on the silicon atom. These results are wholly consistent with the proposed structure.

Similar reaction of 1 with 1,3-cyclohexadiene at 180 °C for 24 h again afforded the double-silylated product. In this reaction, however, a 1:1 mixture of two isomers, *cis*- and *trans*-1-(methylphenylvinylsilyl)-4-(trimethylsilyl)-2-cyclohexene (7a and 7b), was obtained in quantitative yield. Double silylation of various disilanes to unsaturated compounds is well-known.[3-8] However, the reaction of pentamethylphenyldisilane with 2,3-dimethylbutadiene in the presence of the nickel(0) catalyst gave no adduct, and the starting disilane was recovered unchanged. Therefore, it seems likely that the introduction of a vinyl group onto the silicon atom is important for the formation of the double-silylated products, in the present system.

Scheme I illustrates a possible interpretation for the observed products in this system. In the first step, the vinyldisilane 1 adds oxidatively to the nickel catalyst to give the bis(silyl)nickel complex (4). The reaction of the intermediate 4 with dienes gives the adducts 6 and 7. In the presence of the dimethylphenylvinylsilane at higher temperature, the intermediate 4 would isomerize to give

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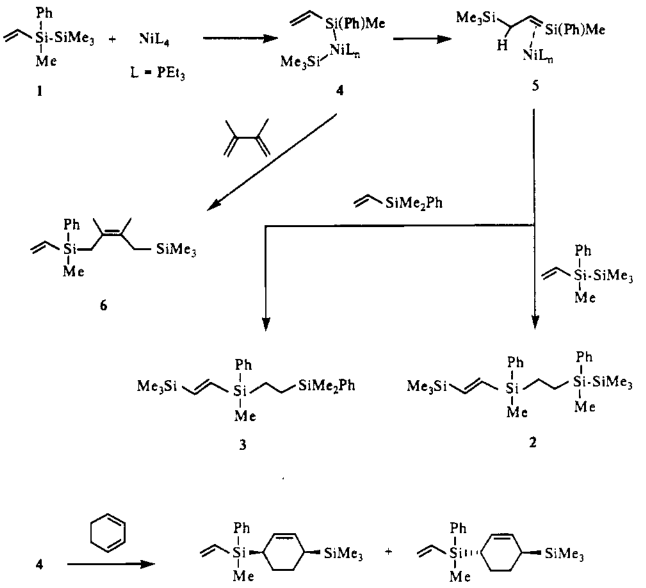
Scheme I



silene–nickel complex 5 via a trimethylsilyl shift from the nickel atom to a vinyl moiety. The regio- and stereospecific addition of the intermediate 5 to the carbon–carbon double bond of coordinated dimethylphenylvinylsilane and reductive elimination of the nickel species would produce the product 3.

In the reaction of the silene 5 with the vinyl mono- and disilane, a hydrogen on the (trimethylsilyl)methyl carbon bound to a silicon–carbon double bond is transferred to the vinyl group to yield adducts 3 and 4. A similar type of reaction has been observed in the photolysis of 1,2,2,2-tetramethylphenylvinyldisilane in the presence of 2,3-dimethylbutadiene.[9]

Experimental Section

All reactions were carried out in a degassed sealed glass tube (ca. 10 cm × 0.8 cm). ^{1}H NMR and ^{13}C NMR spectra were determined with a JEOL Model EX-270 spectrometer using a deuteriochloroform solution containing tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 1600 FT infrared spectrometer. Mass spectra were measured on a Shimadzu Model GCMS-QP 1000 instrument. Tetrakis(triethylphosphine)nickel(0) was prepared by the method reported in the literature[2] just before use.

Dimerization of 1. A mixture of 0.269 g (1.2 mmol) of 1 and 40 mg (7.5×10^{-2} mmol) of tetrakis(triethylphosphine)nickel(0) in 0.5 mL of dry mesitylene in a degassed sealed tube was heated at 220 °C for 24 h. The mixture was treated with a short silica gel column to remove a nickel species. The GLC analysis of the resulting solution using tetradecane as an internal standard shows the presence of dimer 2 (77% yield). Dimer 2 was isolated by preparative GLC. All spectral data were identical with those of the authentic sample.[1]

Reaction of 1 in the Presence of Dimethylphenylvinylsilane. A mixture of 0.3277 g (1.49 mmol) of 1, 0.3001 g (1.85 mmol) of dimethylphenylvinylsilane, and 30 mg (5.6×10^{-2} mmol) of tetrakis(triethylphosphine)nickel(0) in 0.4 mL of mesitylene was heated at 220 °C for 24 h. The resulting mixture was analyzed by GLC as being cross-coupling product 3 (55% yield) and dimer 2 (36% yield), in addition to a small amount of an unidentified product (less than 10% yield). Compound 3 was separated by preparative GLC: MS *m/e* 382 (M$^+$); IR 1428, 1408, 1249, 1132, 836 cm^{-1}; ^{1}H NMR δ 0.06 (s, 9 H, Me$_3$Si), 0.24 (s, 6 H, Me$_2$Si), 0.30 (s, 3 H, MeSi), 0.69–0.71 (m, 4 H, CH$_2$), 6.54 (d, 1 H, H$_a$C=C, J = 23 Hz), 6.79 (d, 1 H, H$_b$C=C, J = 23 Hz), 7.30–7.55 (m, 10 H, phenyl ring protons); ^{13}C NMR δ –5.56 (MeSi), –3.50 (Me$_2$Si), –1.55 (Me$_3$Si), 6.25 (CH$_2$), 7.77 (CH$_2$), 127.71, 128.79, 128.90, 133.67, 133.92, 134.26, 137.78 (two phenyl ring crbons), 146.72, 153.93 (olefin carbons). Anal. Calcd for $C_{22}H_{34}Si_3$: C, 69.11; H, 8.90. Found: C, 68.93; H, 8.90.

Reaction of 1 in the Presence of 2,3-Dimethylbutadiene. A mixture of 0.2012 g (0.915 mmol) of 1, 0.5772 g (2.62 mmol) of 2,3-dimethylbutadiene, and 32 mg (6.0×10^{-2} mmol) of tetrakis(triethylphosphine)nickel(0) in 0.4 mL of mesitylene was treated at 220 °C for 24 h. The mixture was analyzed by GLC as being 6 (92% yield). The product 6 was isolated by preparative GLC: MS *m/e* 302 (M$^+$); IR 1591, 1427, 1402, 1248, 1202, 1112, 1008, 952 cm^{-1}; ^{1}H NMR δ –0.01 (s, 9 H, Me$_3$Si), 0.35 (s, 3 H, MeSi), 1.37 (bs, 2 H, CH$_2$), 1.54 (bs, 3 H, CH$_3$), 1.58 (bs, 3 H, CH$_3$), 1.77 (bs, 2 H, CH$_2$), 5.73 (dd, 1 H, vinylic proton, J_{trans} = 20.1 Hz, J_{gem} = 3.8 Hz), 6.05 (dd, 1 H, vinylic proton, J_{cis} = 14.3 Hz, J_{gem} = 3.8 Hz), 6.32 (dd, 1 H, vinylic proton, J_{trans} = 20.1 Hz, J_{cis} = 14.3 Hz), 7.33–7.54 (m, 5 H, phenyl ring protons); ^{13}C NMR δ –4.3 (MeSi), –0.5 (Me$_3$Si), 21.0 (two CH$_3$), 23.6 (CH$_2$), 26.9 (CH$_2$), 120.9, (C(Me$_a$)dbd), 123.4 (C(Me$_b$)=), 127.7, 128.9, 134.1, 138.0 (phenyl ring carbons), 131.0 (CH$_2$=), 139.45 (CH=). Anal. Calcd for $C_{18}H_{30}Si_2$: C, 71.44; H, 9.99. Found: C, 71.21; H, 9.93.

A solution of 0.162 g (0.74 mmol) of 1, 0.23 g (2.80 mmol) of 2,3-dimethylbutadiene, and 40 mg (7.5×10^{-2} mmol), of tetrakis(triethylphosphine)nickel(0) in 0.4 mL of mesitylene was heated at 150 °C for 24 h. The mixture was analyzed for GLC as being 6 (100% yield).

Reaction of 1 in the Presence of 1,3-Cyclohexadiene. A solution of 0.349 g (1.59 mmol) of 1, 0.392 g (4.90 mmol) of 1,3-cyclohexadiene, and 50 mg (9.4×10^{-2} mmol) of tetrakis(triethylphosphine)nickel(0) in 0.4 mL of mesitylene was heated in a sealed tube at 180 °C for 24 h. The GLC analysis of the mixture showed a single homogeneous peak. The product was isolated by preparative GLC as a 1:1 mixture of 7a and 7b: MS *m/e* 300 (M$^+$); IR 1588, 1425, 1250, 1110, 838 cm^{-1}; ^{1}H NMR δ –0.07 (s, 9 H, Me$_3$Si), –0.06 (s, 9 H, Me$_3$Si), 0.35 (s, 3 H, MeSi), 0.36 (s, 3 H, MeSi), 1.31–2.17 (m, 12 H, four CH$_2$ and four CH), 5.64 (bs, 4 H, CH=CH), 5.73 (dd, 1 H, vinylic proton, J_{trans} = 18 Hz, J_{gem} = 6 Hz), 5.77 (dd, 1 H, vinylic protein, J_{trans} = 18 Hz, J_{gem} = 6 Hz), 6.07 (dd, 1 H, vinylic proton, J_{cis} = 15 Hz, J_{gem} = 6 Hz), 6.10 (dd, 1 H, vinylic proton, J_{cis} = 15 Hz, J_{gem} = 6 Hz), 6.37 (dd, 1 H, vinylic proton, J_{trans} = 18 Hz, J_{cis} = 15 Hz), 6.39 (dd, 1 H, vinylic proton, J_{trans} = 18 Hz, J_{cis} = 15 Hz), 7.31–7.60 (m, 10 H, phenyl ring protons); ^{13}C NMR δ –6.4 (MeSi), –6.3 (MeSi), –2.6 (two Me$_3$Si), 23.3 (CH$_2$), 23.4 (CH$_2$), 23.5 (two CH), 24.8 (CH), 24.9 (CH), 26.5 (two CH$_2$), 125.2 (two C(H$_a$)=), 126.9 (two C(H$_b$)=), 127.8, 129.1, 134.5, 136.5 (two phenyl ring carbons), 133.9 (two CH$_2$=), 135.9 (two CH=). Anal. Calcd for $C_{18}H_{28}Si_2$: C, 71.92; H, 9.39. Found: C, 72.00; H, 9.32.

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Registry No. 1, 66534-99-4; 2, 123495-41-0; 3, 136839-24-2; 6, 136839-25-3; 7a, 136839-26-4; 7b, 136839-27-5; 2,3-dimethylbutadiene, 513-81-5; 1,3-cyclohexadiene, 592-57-4; dimethylphenylvinylsilane, 1125-26-4.

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