Preparation, Structure, and Reactivity of Functionalized Organosilicon Compounds

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Preparation, structure, and reactivity of (alkoxysilyl)lithium, (alkoxy)oligosilanes, and penta-coordinate alkoxysilane have been investigated. These functionalized organosilicon compounds containing a-heteroatom substituents exhibit remarkable reactivities compared to ordinary organosilicon compounds.

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(1) The Chemistry of Silylenoids: Preparation and Reactivity of (Alkoxysilyl)lithium [1]

We report the first results of silylenoid chemistry, analogous to carbenoid chemistry. (t-Butoxysilyl)lithium (t-BuO)Ph2SiLi (1) prepared from (t-butoxysilyl)stannane with n-BuLi in THF is stable at -78 °C. In the presence of 12-crown-4, 1 is stable as silyl anion even at 0 °C and reacts with electrophiles only. In contrast to this, 1 exhibits the ambiphilic reactivity and undergoes at 0 °C self-condensation smoothly to form (t-BuO)Ph2SiPh2SiLi or butylation in the presence of an excess amount of n-BuLi and TMEDA to form n-BuPh2SiLi. The ambiphilic activities of 1 could be accounted for by contribution of two extreme structures, that is, a nucleophilic silyl anionic structure and an electrophilic silylenoid structure. In the latter, the electropositive lithium atom bound to silicon ionizes and activates the silicon-oxygen bond so that the silicon becomes susceptible to the nucleophilic attack.

(2) Palladium-Catalyzed Skeletal Rearrangement of (Alkoxysilyl)oligosilanes via Silylene-Transfer [2]

Poly(alkoxy)trisilanes and tetrasilanes have been found to undergo clean skeletal rearrangement in the presence of Pd(PPh3)4 as a catalyst at 80 - 140 °C in the fashion that the internal silylene moiety is transferred to the terminal positions. Ten substrates have...
been examined. Typically, 1,2,3-(MeO)4Me4SiS, 1,1,2,2,3-(MeO)4Me4SiS, 1,2,3-(MeO)4Me2SiS, and 1,2-(MeO)3Me6SiS, are converted into the 1,1,1,3-, 1,1,3,3-, 1,1,3-, and 1,1-isomers, respectively, in quantitative yields: the reactivity decreases roughly in this order. In a deuterium-labeled study, 1,1,2,3-(MeO)4-3,3-(CD3)2Me2SiS gives 1,1,3,3-(MeO)4-2,2-(CD3)2Me2SiS exclusively, no CDs/CHs random exchange being observed. A tetrasilane 1,2,3,4-(MeO)4Me6Si4 is also transformed into the 1,1,4,4-isomer. A proposed mechanism involves silylene-transfer from the internal position to the terminal position(s) through the following key steps: oxidative addition of the Si-Si bond to Pd(0) and subsequent α-elimination to a bis(silyl)(silylene)Pd complex, stabilized by the intramolecular coordination of alkoxy group(s) to the silylene center. The novel skeletal rearrangement may be useful for the structural modification of polyfunctionalized polysilanes of much current interest.

Pentacoordinate ethoxydisilane 2, which contains the 8-dimethylamino-1-naphthyl group and the ethoxy group on the same silicon atom, and the tetracoordinate counterpart 3 have been prepared. The X-ray structure analysis of 2 reveals that the geometry of the particular silicon atom is deformed from tetrahedral to pseudo-trigonal bipyramidal with the ethoxy group and the amino group at two pseudo-apical positions, having the N1···Si1 distance 2.969(3) Å and the N1···Si1-O1 angle 171.36(9)°. This compound has a normal Si1-Si2 distance 1.891(3) Å. Compound 3 is oxygen-stable.

References