Recent Chemistry on Silylenoids

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Over the past decades, a few novel silylenoids have been the subject of an extensive study. Silylenoids are species showing their amphiphilic properties towards electrophiles and nucleophiles, respectively, which are the silicon-analogues of carbenoids. Recently, a few stable silylenoids have been reported, including $TsiSiX_2Li$ (Tsi = $C(SiMe_3)_3$, X = Cl, Br), $(Mes)_2Si(SMes)Li$ and $(R_3Si)_2SiFLi$ (R_3Si = *t*-Bu_2MeSi). Such stable silylenoids having a halogen atom, we reported, have been particularly important in the studies of their various reactivities such as reductions, substitutions, additions, transmetallations, etc. In this context, we now report some unprecedented examples of the reactions of halosilylenoids with various aldehydes, ketones, and olefins. (Tsi)chlorosilylenoid having the bulky substituent was synthesized by the reduction of trichlorotrisylsilane with 2 equivalent of LiNp (lithium naphthalenide), reacted with aldehydes such as acetaldehyde and benzaldehyde to give 2,4-dioxasilolane and 2,5-dioxasilolane, respectively. The direct addition of an aldehyde to a silaoxirane intermediate is proposed as a plausible mechanism based on a theoretical study. (Tsi)chlorosilylenoid also reacted with ketones like acetophenone and benzil to give the corresponding 2,5-dioxasilolanes and silylethers, respectively. It is worth mentioning that these reactions of halosilylenoids can be used as new synthetic routes for functional silaheterocyles.

In this presentation, the further reactions of halosilylenoids with olefins, imines as well as various ketones will be discussed in detail.