Synthesis of Kinetically Stabilized Silaneselone and Silanetellone

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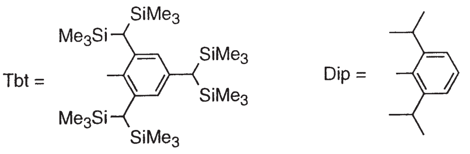
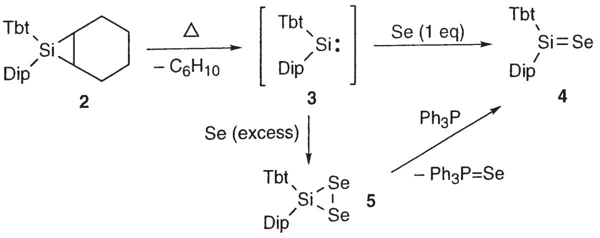
Kinetically stabilized silaneselone [Tbt(Dip)Si=Se (**4**); Tbt=2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Dip=2,6-diisopropylphenyl] and silanetellone [Tbt(Dip)Si=Te] were synthesized by direct chalcogenation of Tbt(Dip)M: (M=Si, Ge) with elemental chalcogen. Deselenation of Tbt(Dip)$SiSe_2$ also gave **4**. Metallanetellones [Tbt(Dip)M=Te; M=Si, Ge] were also synthesized by the reaction of Tbt(Dip)MLi_2 (M=Si, Ge) with $TeCl_2$, which is a new synthetic method for heavy ketones.

Since ketones play very important roles in organic chemistry, much interest has been focused on the chemistry of double-bond compounds between heavier group 14 and group 16 elements (we refer to this family of heavier congeners of ketones as "heavy ketones").[1] However, the chemistry of heavy ketones had been less explored due to their extremely high reactivities. In recent years, however, we have reported the syntheses of a variety of stable examples of kinetically stabilized heavy ketones[2–4] by taking advantage of efficient steric protection group, Tbt.[5] As for silicon-containing heavy ketones, only a silanethione bearing Tbt and Tip groups [Tbt(Tip)Si=S (**1**); Tip=2,4,6-triisopropylphenyl] was isolated as a stable compound.[2] Although some examples are known for silaneselones stabilized by the intramolecular coordination of a nitrogen atom[6] and transient silaneselones as reactive intermediates,[7] no coordination-free examples have been synthesized yet for silaneselones and silanetellones so far. Here, we present the synthesis of stable silaneselone and silanetellone by taking advantage of kinetic stabilization afforded by the combination of Tbt and Dip groups.



The stable silanethione **1** was synthesized by the desulfurization of the corresponding tetrathiasilolane, Tbt(Tip)SiS_4.[2] However, this type of synthetic method cannot be applied to the synthesis of silaneselone, since the preparation of tetraselenasilolane [Tbt(Tip)$SiSe_4$] was unsuccessful due to its extreme instability. Then, we have examined an alternative synthetic route to silaneselone via direct selenation of a sterically hindered silylene. When a C_6D_6 solution of silanorcarane **2**, which is known to give the corresponding silylene **3** by thermolysis,[8] was heated in the presence of equimolar amount of selenium at 100 °C for 82 h in a sealed tube, the resulting reddish orange solution showed peaks at 174 and 635 ppm in the ^{29}Si and ^{77}Se NMR spectra, respectively. The characteristically down-fielded ^{29}Si NMR chemical shift strongly indicates the existence of the sp^2 silicon center, *i.e.*, the formation of the stable silaneselone **4**. Although **4** was a main product in this reaction as judged by NMR, the reaction mixture contained various by-products and it was difficult to isolate silaneselone **4** in a pure form.



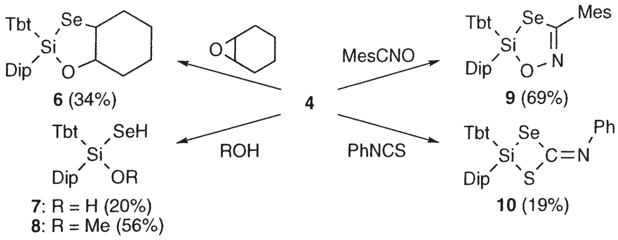
Scheme 1.

On the other hand, the reaction of **2** with excess of elemental selenium in C_6D_6 at 120 °C for 19 h in a sealed tube resulted in almost quantitative formation of diselenasilirane **5**[9] having a novel $SiSe_2$ ring system (Scheme 1). The ^{29}Si and ^{77}Se NMR spectra of **5** showed signals at -44 and -174 ppm, respectively. The UV/vis spectrum of **5** in THF showed an absorption maximum at 509 nm most likely assignable to the n-σ^* absorption of the Se-Se moiety in **5**. The considerable bathochromic shift observed for 5 should be of interest as that for highly strained diselenasilirane skeleton in comparison with those for 1,4-bis[tris(trimethylsilyl)methyl]tetraselenadisilabicyclo[2.1.1]hexane [450 nm (ε 60) in hexane][10] and typical diselenides [329 nm (ε 1.1×10^3) for diphenyl diselenide in ethanol[11]].

Since **5** was considered to be a useful precursor of **4**, deselenation of **5** was next examined with Ph_3P in THF at room temperature resulting in the change of the color from red to orange. The ^{29}Si and ^{77}Se NMR spectra ($\delta_{Si} = 174$, $\delta_{Se} = 635$; in C_6D_6) of the resulting material are identical with those of **4** formed in the above-mentioned direct selenation of **3**. The electronic spectrum of the reaction mixture in THF showed an absorption maximum at 456 nm, which was assignable to that for the n-π^* transition of the Si=Se moiety. These results indicate that the formation of silaneselone **4** can also be performed by the deselenation method. Although the formation of by-products was considerably suppressed in this transformation, the isolation of **4** as pure crystals has not been achieved yet even by this new method.

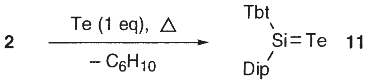
The reaction mode of **4** was found to be almost similar to that of other heavy ketones.[1] Silaneselone **4** underwent 1,2-addition, C–O insertion, [2 + 3]cycloaddition, and [2 + 2]cycloaddition as can be seen in the reactions with ROH (R=H, Me), cyclohexene oxide, mesitonitrile oxide, and phenyl isocyanate, respectively (Scheme 2). Although the adducts **6-9** are stable in air and moisture and can be chromatographically purified, the [2 + 2]adduct **10** is liable to be gradually hydrolyzed to give **7** and phenyl isothiocyanate on exposure to air. The mechanism for the hydrolysis of **10** is most likely explained by initial attack of a water molecule to the silicon atom, followed by the extrusion of phenyl isothiocyanate in preference to phenyl isoselenocyanate.

As an extension of the above-mentioned chemistry, synthesis of a silanetellone was also examined by the thermolysis of **2** in the



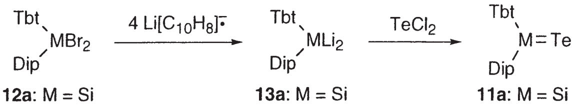
Scheme 2.

presence of elemental tellurium. When the mixture of **2** and elemental tellurium in C_6D_6 was heated in a sealed tube at 90 °C for 5 days and then at 75 °C for 25 days, the color of the reaction mixture turned dark green suggesting the formation of silanetellone **11a**. Although the UV/vis spectrum of the reaction mixture in THF showed absorption maximum at 593 nm assignable to the n-π^* transition of a silanetellone, the ^{29}Si NMR spectrum showed no signal assignable to the sp^2 silicon probably because of the low yield of **11a**.



$$\mathbf{2} \xrightarrow[-\,C_6H_{10}]{\text{Te (1 eq)},\ \Delta} \text{Tbt(Dip)Si=Te} \quad \mathbf{11a} \qquad (1)$$

In order to generate **11a** more effectively, we developed another useful synthetic method via the overcrowded diaryldilithiosilane **13a**, which has recently been developed by us as a key reagent in the synthesis of the first stable silacyclopropabenzene.[12] Reaction of **13a**, prepared by the exhaustive reduction of dibromosilane **12a**,[12a] with $TeCl_2$ in THF at −78 °C gave the expected silanetellone **11a** as a green solid (Equation 2). The ^{29}Si and ^{125}Te NMR spectra of this reaction product in C_6D_6 showed characteristic signals in low-field regions ($\delta_{Si} = 171$, $\delta_{Te} = 731$) and the UV/vis spectrum ($\lambda_{max} = 593$ nm in benzene) was almost identical with that of the above-mentioned silanetellone formed by the thermal reaction of **2** with elemental tellurium. It should be noted that **11a** is the first example of a stable silanetellone spectroscopically identified. The n-π^* transisions of silanethione **1** (396 nm in hexane), silaneselone **4** (456 nm in THF) and silanetellone **11a** (593 nm in benzene) are red-shifted in the order of **1**, **4**, and **11a** as in the case of other heavy ketones series.[1b]



$$\text{Tbt(Dip)MBr}_2 \xrightarrow{4\,Li[C_{10}H_8]^{-\bullet}} \text{Tbt(Dip)MLi}_2 \xrightarrow{TeCl_2} \text{Tbt(Dip)M=Te} \qquad (2)$$

12a: M = Si **13a**: M = Si **11a**: M = Si
12b: M = Ge **13b**: M = Ge **11b**: M = Ge

The successful synthesis of **11a** here described naturally prompted us to apply this methodology to the synthesis of other heavy ketones, and as an example we have examined the synthesis of a stable germanetellone via the corresponding dilithiogermane intermediate. Thus, dilithiogermane **13b**,[13] derived from dibromogermane **12b** by the exhaustive reduction with lithium naphthalenide, was allowed to react with $TeCl_2$ in THF at −60 °C to give the corresponding germanetellone **11b** quantitatively (Equation 2).[14] The ^{125}Te NMR chemical shift (1194 ppm in C_6D_6) for **11b** is almost similar to that of Tbt(Tip)Ge=Te ($\delta_{Te} = 1143$ ppm in C_6D_6), which was reported as the first example of a stable diarylgermanetellone.[3c]

In summary, we have succeeded in the synthesis and spectroscopic characterization of kinetically stabilized silaneselone **4** and silanetellone **11a**. The isolation of the newly obtained heavy ketones as crystals and their crystallographic analysis are currently in progress.

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Dedicated to Prof. Teruaki Mukaiyama on the occasion of his 70th birthday.

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9 **5**: ^{1}H NMR (C_6D_6, 500 MHz) δ 0.19 (s, 18H), 0.20 (s, 18H), 0.29 (s, 18H), 1.21 (d, $J = 6.8$ Hz, 6H), 1.32 (d, $J = 6.8$ Hz, 6H), 1.51 (s, 1H), 2.89 (br s, 1H), 3.37 (br s, 1H), 3.97 (sept, $J = 6.8$ Hz, 2H), 6.60 (s, 1H), 6.73 (s, 1H), 7.11 (d, $J = 7.8$ Hz, 2H), 7.20 (t, $J = 7.8$ Hz, 1H); ^{13}C NMR (C_6D_6, 68 MHz) δ 1.2 (q), 2.0 (q), 2.1 (q), 23.1 (q), 27.6 (d), 27.9 (q), 28.0 (d), 31.3 (d), 36.6 (d), 122.7 (s), 124.4 (d × 2), 129.7 (d), 131.1 (d), 136.5 (s), 146.3 (s), 153.6 (s), 154.0 (s), 154.3 (s); ^{29}Si NMR (C_6D_6, 99 MHz) δ −44.3, 2.3, 2.8, 3.3; ^{77}Se NMR (C_6D_6, 51 MHz) δ −174.

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14 **11b**: ^{1}H NMR (C_6D_6, 400 MHz) δ 0.14 (s, 18H), 0.19 (s, 18H), 0.24 (s, 18H), 1.28 (d, $J = 6.5$ Hz, 6H), 1.36 (d, $J = 6.5$ Hz, 6H), 1.48 (s, 1H), 3.48 (br s, 1H), 3.63 (sept, $J = 6.5$ Hz, 2H), 3.87 (br s, 1H), 6.48 (br s, 1H), 6.64 br (s, 1H), 6.99 (d, $J = 7.8$ Hz, 2H), 7.20 (t, $J = 7.8$ Hz, 1H); ^{13}C NMR (C_6D_6, 100 MHz) δ 1.5 (q), 2.2 (q), 2.5 (q), 22.5 (q), 27.1 (q), 28.6 (d), 28.9 (d), 32.3 (d), 34.9 (d), 125.3 (d × 2), 130.5 (d), 131.0 (d), 146.6 (s), 147.1 (s), 148.9 (s), 149.4 (s), 150.1 (s), 157.8 (s); ^{125}Te NMR (C_6D_6, 95 MHz) δ 1194.