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The pinnacle of the ancient sundial is pointing a dioxasilolane, a functional silaheterocycle, which is produced from the reaction of a stable chlorotrisylsilylenoid with acetophenone. The sundial metaphorically represents that silylenoid (R_2SiMX , M = metal, X = halogen) chemistry is in progress.

Title: Reactivities of chlorotrisylsilylenoid with ketones

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Reactivities of chlorotrisylsilylenoid with ketones†

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Chlorotrisylsilylenoid 1 reacted with both acetophenone and benzil to give the corresponding 2,5-dioxasilolanes and silylethers, respectively.

Silylenoids (R₂SiMX) are species in which an electropositive metal (M, usually alkali metal) and a leaving group (X, usually halogen) are bound to the same silicon atom, and have amphiphilic properties. The reactivities of silylenoids are similar to those of silylenes (R₂Si:).¹⁻⁶ Only a few stable silylenoids including (tBuO)Ph₂SiLi,² (Mes)₂Si(SMes)Li,³ (Me₃Si)₂Si(OMe)K·crownether⁴ and $(R_3Si)_2SiFLi^5$ $(R_3Si = t-Bu_2MeSi)$ have been reported and there are no reports on the reaction of a silvlenoid with ketones. Recently we reported the synthesis of halosilylenoids $TsiSiX_2Li$ (Tsi (trisyl) = C(SiMe_3)_3, X = Br, Cl) and their reactivities with various alcohols, dienes, aldehydes, alkyl halides, silyl halides, aryllithiums, arylmagnesium bromides and lithium naphthalenide.⁶ Since stable halosilylenoids have two halogens and one lithium, reactions such as substitution, addition, transmetalation and reduction are all possible. In this paper we report unprecedented examples of the reaction of a chlorotrisylsilylenoid with a monoketone and a diketone.

To the stable chlorosilylenoid **1** having a bulky Tsi group, which was formed by the reduction of trichlorotrisylsilane with two equivalents of lithium naphthalenide, was added an excess of acetophenone at -78 °C. Following 1 h stirring at that temperature, treatment of the reaction mixture with excess MeOH gave the products 2,5-dioxasilolane (**2**) and silylalkylether (**3**) in 43% and 17% yields (Scheme 1).‡



Scheme 1 Reaction of chlorosilylenoid with acetophenone.

Compound **2**, which was stable to air and moisture, was obtained as a colorless single crystal from recrystallization in *n*-hexane at room temperature.§ The molecular structure of **2** was characterized by X-ray crystallography (Fig. 1). All atoms except a quaternary carbon in the Tsi group appeared to be disordered with two possible orientations in a ratio of 0.77 to 0.23. The sum of the interior angles of **2** was 533.0°, indicating a nearly planar structure of the five-membered 2,5-dioxasilolane ring. Interestingly, only one of the possible isomeric structures,



Fig. 1 ORTEP drawing of **2** shown with 30% thermal ellipsoid. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–Cl1 = 2.091(1), Si1–Cl(Tsi) = 1.847(3), Si1–O1 = 1.640(2), Si1–O2 = 1.646(2); O1–Si1–O2 = 96.65(9).

having a *trans-trans* conformation of Tsi-Ph^a–Ph^b was observed. This stereo- and regio-selectivity is evidently due to the bulky substituents.⁷

A possible mechanism for the formation of **3** can be explained by the Brook rearrangement⁸ (Scheme 2). Nucleophilic attack of silicon atom of **1** to acetophenone generated a silylalkoxide, which underwent further reaction *via* a [1,2]-silyl migration from carbon to oxygen to give carboanion **4**. Species **4** did not undergo an intramolecular cyclization, possibly due to the large Si–O–C angle. Treatment of **4** with excess MeOH and MeOD gave products **3** and deuterated **3**.



Scheme 2 Possible mechanisms for the formation of 2 and 3.

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The formation of 2 can be explained by two plausible mechanisms. Firstly, a highly reactive intermediate oxasilacyclopropane9 was generated by intramolecular cyclization of the silvlalkoxide (pathway i), followed by a direct insertion of an acetophenone into a Si-C bond of the oxasilacyclopropane to give compound 2. A silacarbonyl ylide9c-f,10 (TsiClSi--O+=CMePh), formed through the heterolytic cleavage of oxasilacyclopropane, might be involved in producing the 2,5-dioxasilolane. However, the previous DFT calculation revealed that the silacarbonyl ylide ((H₃Si)₃CClSi-O⁺=CMeH) was less stable than the corresponding oxasilacyclopropane formed by the reaction of the silvlenoid with acetaldehyde.^{6d} Jutzi and co-workers also suggested that oxasilacyclopropanes formed from the reaction of decamethylsilicocene with aldehydes, would be key intermediates in silvlene chemistry, rather than silacarbonyl ylides.⁹⁶ An alternative pathway to 2 is the formation of silvlether alkoxide by nucleophilic attack of carboanion of 4 on an acetophenone, followed by intramolecular cyclization (pathway ii).

In the reaction of chlorosilylenoid **1** with the α -diketone benzil, the reaction mixtures were quenched by H₂O and MeOH to give compounds **5** and **6** in 56% and 62% yields (Scheme 3). Compound **6** was isolated through flash column chromatography and then obtained as colorless crystals by recrystallization from *n*-hexane. The structure of **6** was characterized by X-ray crystallography (Fig. 2). The sum of the interior angles around the ring of **6** was 523.3°, indicating a slightly distorted structure of the five membered heterocycle.



Scheme 3 Reaction of chlorosilylenoid with benzil.

For the reaction of 1 with benzil, we propose the following mechanism (Scheme 4). Organolithium intermediate 7 was initially generated through a similar mechanism to the formation of 4. From the trapping experiment of species 7 with H_2O and D_2O , the hydrolyzed products 5 and deuterated 5 were obtained, respectively. Interestingly the trapping of 7 by MeOH showed a



Scheme 4 Possible mechanisms for the formation of 5 and 6.



Fig. 2 ORTEP drawing of **6** shown with 30% thermal ellipsoid. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–Cl1 = 2.080(2), Si1–Cl6(Tsi) = 1.834(4), Si1–O1 = 1.650(3), Si1–O2 = 1.668(3); Cl1–Si1–Cl6(Tsi) = 111.6(2).

different result from that with H_2O . Addition of MeOH to the reaction mixtures containing intermediate 7 afforded 1,3-dioxa-2-silacyclopentane, 6, which was formed through the nucleophilic addition of LiOMe to the unreacted carbonyl carbon followed by cyclization. To prove this proposed mechanism, we carried out the reaction of the isolated compound 5 with LiOMe. As anticipated, compound 6 was formed.

It is worth mentioning that these reactions of a silylenoid with diketone are different from those of silylenes. In the reactions of silylenes with α -diketones, 1,3-dioxa-2-silacyclopent-4-enes were formed by a concerted [2 + 1] cycloaddition process.¹¹ By comparison, the silylenoid reaction took place stepwise to produce a silylether type compound which underwent further reactions to give 2,5-dioxasilolane. Our ongoing work will address the reactivities of silylenoid with various ketones, such as acetone, β -diketones, naphthoquinone and α , β -unsaturated ketones. We wish to establish new synthetic routes for functional silahetero-cylcles.

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Notes and references

‡ Synthesis of 2 and 3: naphthalene (1.28 g, 10 mmol) dissolved in THF (40 mL) was added to Li (0.060 g, 8.7 mmol) at room temperature. After stirring for 3 h at room temperature, LiNp (lithium naphthalenide) was obtained as a dark green solution. LiNp in THF was added slowly to TsiSiCl₃ (1.46 g, 4.0 mmol) in THF (40 mL) at -78 °C using cannula technique within 10 min. The solution was stirred for 12 h at the same temperature; all the starting reactants were consumed to give chlorosilylenoid 1. To the dark brown reaction mixture was added an excess of acetophenone (4.7 mL, 40 mmol) at -78 °C. After 1 h, to the reaction mixture was added an excess of MeOH. The final reaction mixture was slowly warmed to room temperature, and then the solvent was evaporated under reduced pressure. After the sublimation of naphthalene, to the resulting viscous light yellow oil was added *n*-hexane (100 mL) and then precipitated species were removed by filtration. The crude material was purified by silica gel chromatography (n-hexane) to afford 2 (0.92 g, 1.7 mmol) as a white powder and 3 (0.31 g, 0.68 mmol) as a colorless oil. Spectral data for 2: colorless crystal (mp = 194-196 °C). ¹H NMR (400 MHz, chloroform-d): δ 0.47 (s, 27H), 1.36 (s, 3H), 1.39 (s, 3H), 7.27-7.66 (m, 10H). ¹³C NMR (100 MHz, chloroform-d): δ 5.3 (SiCH₃), 6.5 (C(Si(CH₃)₃)₃), 29.8 (CH₃), 31.3 (CH₃), 88.0 (OC), 88.8 (OC), 125.5, 126.7, 126.9, 127.0, 127.7, 127.8 (Ph-C), 145.5, 145.8 (Ph-ipso-C). GC-MS: m/z (%) 534 (M⁺, 3.0), 519 (14.7), 295 (100), 275 (34.2), 187 (46.4), 105 (50.4), 73 (23.2). HRMS: $C_{26}H_{43}ClO_2Si_4$ 534.2029 (calcd), 534.2028 (found). Anal. Calcd for C₂₆H₄₃ClO₂Si₄: C, 58.32; H, 8.09; O, 5.98. Found: C, 58.29; H, 8.11; O, 5.89. Spectral data for 3: Colorless oil. ¹H NMR (400 MHz, chloroform-d): $\delta 0.30$ (s, 27H), 1.60 (d, J = 6.44, 3H), 5.29 (q, J = 6.44, 1H), 7.28–7.39 (m, 5H). ¹³C NMR (100 MHz, chloroform-*d*): δ 4.3 (SiCH₃), 7.5 (C(Si(CH₃)₃)₃), 24.8 (CH₃), 74.1 (OC), 128.2, 127.8, 128.2 (Ph-C), 143.0 (Ph-ipso-C). GC-MS: m/z (%) 449 (M+-1, 1.3), 331 (3.4), 295 (3.9), 207 (6.0), 105(100), 73 (12.3). HRMS: C₁₈H₃₅Cl₂OSi₄ 449.1142 (M⁺-1, calcd), 449.1143 (found). Anal. Calcd for C₁₈H₃₆Cl₂OSi₄: C, 47.86; H, 8.03; O, 3.54. Found: C, 47.90; H, 8.09; O, 3.57.

Synthesis of 5 and 6: to the product mixture of chlorosilvlenoid 1 was added an excess of benzil (4.2 g, 20 mmol) in a manner similar to that described above. After 6 h, to the reaction mixture was added an excess of H₂O and MeOH. The crude material was purified by silica gel chromatography (n-hexane) to afford 5 and 6 in 56% (1.2 g, 2.2 mmol), and 62% (1.3 g, 2.5 mmol), respectively. White powder 6 was recrystallized from *n*-hexane to give colorless crystals. Spectral data for 5: colorless oil. ¹H NMR (400 MHz, chloroform-d): δ0.32 (s, 27H), 6.55 (s, 1H), 7.29–7.93 (m, 10H). ¹³C NMR (100 MHz, chloroform-*d*): δ 4.2 (SiCH₃), 7.9 (C(Si(CH₃)₃)₃), 128.6, 128.7, 128.8, 128.9 (Ph-C), 133.2 (CH), 135.0, 136.0 (Ph-ipso-C), 194.3 (C=O). GC-MS: m/z (%) 525 (M+-15, 3.5), 504 (3.4), 435 (28.4), 195 (56.5), 167 (54.9), 105 (100), 73 (43.2). HRMS: C₂₄H₃₉Cl₂O₂Si₄ (M⁺+1) 541.1404 (calcd), 541.1409. Anal. Calcd for C24H38Cl2O2Si4: C, 53.20; H, 7.07; O, 5.91. Found: C, 53.08; H, 7.11; O, 5.85. Spectral data for 6: colorless crystal. ¹H NMR (400 MHz, chloroform-d): $\hat{\delta}$ 0.49 (s, 27H), 3.03 (s, 3H), 5.04 (s, 1H), 7.31-7.54 (m, 10H). 13C NMR (100 MHz, chloroformd): δ 4.6 (SiCH₃), 4.7 (C(Si(CH₃)₃)₃), 50.4 (OCH₃), 84.4 (OCH), 106.1 (OCO), 127.4, 127.5, 127.8, 128.0, 128.1, 128.3, 128.9, 129.3 (Ph-C), 135.9, 139.8 (Ph-ipso-C). GC-MS: m/z (%) 536 (M+, 13.5), 521 (5.5), 400 (10.8), 295 (47.5), 167 (88.9), 73 (100). HRMS: C₂₅H₄₁O₃Si₄Cl 536.1821 (calcd), 536.1823 (found). Anal. Calcd for C25H41O3Si4Cl: C, 55.88; H, 7.69; O, 8.93. Found: C, 55.77; H, 7.72; O, 8.85.

§ Crystal and structure refinement data for **2**: $C_{26}H_{43}ClO_2Si_4$, M = 535.41, monoclinic, $P2_1/n$, a = 11.5132(4), b = 9.1353(3), c = 28.9123(10) Å, $\alpha = \gamma = 90.00^{\circ}, \beta = 90.532(2)^{\circ}, V = 3040.76(18) \text{ Å}^3, T = 296 \text{ K}, Z =$ 46 436 independent reflections (R(int) = 0.0346), $R_1 = 0.0588$ (observed data), w $R_2 = 0.1806$ (all data). Crystal and structure refinement data for 6: $C_{25}H_{41}O_{3}Si_{4}Cl$, M = 536.38, monoclinic, $P2_{1}/c$, a = 17.846(2), b =9.1122(12), c = 18.625(2) Å, $\alpha = \gamma = 90.00^{\circ}$, $\beta = 91.569(2)^{\circ}$, V = 3027.6(7)Å³, T = 273 K, Z = 44583 independent reflections (R(int) = 0.0400), $R_1 =$ 0.0669 (observed data), $wR_2 = 0.2182$ (all data). Several atoms (Si1, Si3, Si4, C22, C25, and Cl1) appeared to be disordered (a ratio of each of disorder components = 0.81 : 0.19).

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