at room temperature for the $[Ru(4,4'-(CO_2Et)_2bpy)_3]^{2+}$ species will be completed shortly and reported later.

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Hexaalkylcyclotrisilanes $(R_2Si)_3$: Hexakis(1-ethylpropyl) and Hexaisopropyl Derivatives

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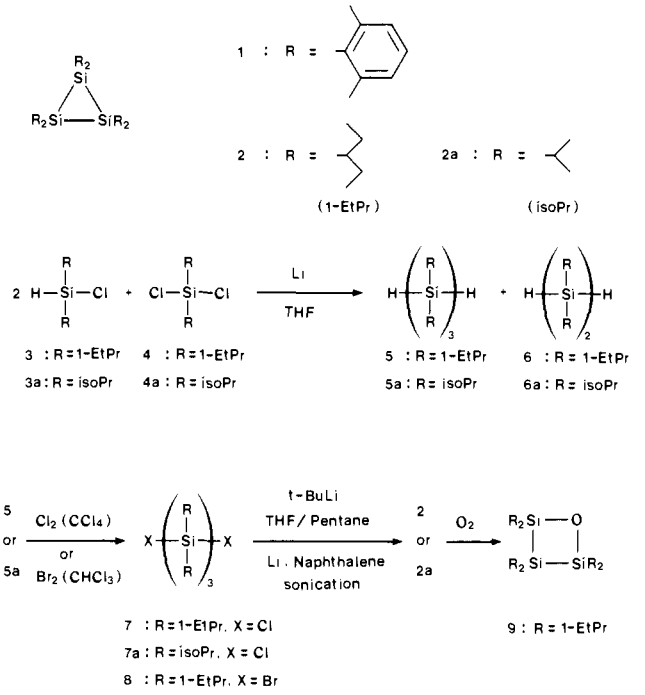
Hexakis(2,6-dimethylphenyl)cyclotrisilane (**1**)[1] represents the first and thus far only compound that incorporates the silicon three-membered ring system. While the strain imposed upon this small ring is clearly and uniquely manifested in its chemical behavior, the full *aryl* substitution in **1** causes significant perturbation of the electronic structure intrinsic to the cyclotrisilane system.[2] With the purpose of eliminating this complication, the synthesis of the titled *alkyl* (rather than aryl) substituted derivatives (**2** and **2a**) has been contemplated. We record herein the high-yield synthesis and photochemical reaction of these compounds. In the present cases, the modified Kipping reaction successfully used for the synthesis of **1** is of no avail,[1,3] but reductive cyclization of 1,3-dichlorohexaalkyltrisilanes *under the conditions precisely specified below* has now been found to be highly efficient (80–90%) and also to have general applicability for those having moderately bulky alkyl substituents. Compound **2** undergoes photofragmentation to yield the corresponding disilene and silylene species.

Synthesis of 2. A mixture of chlorobis(1-ethylpropyl)silane (**3**) (50 mmol) and dichlorobis(1-ethylpropyl)silane (**4**) (23 mmol) in tetrahydrofuran (THF) (120 mL) is allowed to react with lithium (dispersion, 0.132 mol) at 0 °C for 3 h and then at room temperature overnight.[4] Two products that result from this reaction are 1,1,2,2,3,3-hexakis(1-ethylpropyl)trisilane (**5**)[5] (12.1 mmol, bp 196 °C (0.18 torr)) and 1,1,2,2-tetrakis(1-ethylpropyl)disilane (**6**)[5] (4.36 mmol, bp 120 °C (0.18 torr)) (see Scheme I). Chlorination of **5** under standard conditions proceeds smoothly at 0 °C to provide in 91% yield 1,3-dichloro-1,1,2,2,3,3-hexakis(1-ethylpropyl)trisilane (**7**)[5] (bp 175 °C (0.02 torr)). The corresponding dibromo compound (**8**)[5] (bp 196–202 °C (0.015 torr)) is also obtained in an analogous manner (90% yield).

Reductive cyclization of **7** has been examined extensively. The course of the reduction is highly sensitive to several experimental parameters, and indeed the exclusive formation of the cyclotrisilane **2** can be achieved only with a specific combination of reductants and solvent system. Thus, to a solution of **7** (1.73 mmol) in a mixed solvent (4 mL of THF and 32 mL of pentane) is added at −78 °C a 2 M solution of *tert*-butyllithium (1.72 mmol) in pentane; the resulting mixture is stirred for 45 min at −78 °C and then warmed to room temperature over a period of 2 h. Lithium (dispersion, 4.5 mmol) and naphthalene (0.19 mmol) are simultaneously added, and the reaction flask is immersed in an ultrasonic bath maintained at 40–45 °C. After 18 h, another portion of lithium (dispersion, 1.4 mmol) is added and sonication continued for another 21 h. The reaction is now completed,[6] and the usual workup including flash chromatography provides colorless crystals, mp 240 °C dec. The assignment of the cyclotrisilane structure to this product is based on its spectral properties: high-resolution mass spectrum (electron impact) calculated for $C_{30}H_{66}Si_3$, m/z 510.4472, found, m/z 510.4463, M^+ 510 (13%), 440 (1.2), 370 (8.0), 340 (3.9), 300 (49), 271 (11), 270 (7.9), 269 (13), 230 (100), 201 (15), 200 (22), 199 (22), 169 (49), 160 (49), 131 (67), 130 (36), 129 (90); ^1H NMR (250 MHz, C_6D_6) δ 1.12 (36 H, t, J = 7.3 Hz, CH_3), ca. 1.12 (6 H, CH), 1.69 (12 H, ddq, J = 7.3, 14.6, 7.3 Hz), 1.93 (12 H, ddq, J = 4.3, 14.6, 7.3 Hz); ^{13}C NMR (67.8 MHz, C_6D_6) δ 15.73 (q, J = 121 Hz), 27.84 (t, J = 129 Hz), 30.04 (d, J = 118 Hz); IR (KBr) 2955, 2920, 2865 (ν C–H), 1460, 1375 (ν C–H) cm^{-1}; UV (methylcyclohexane) λ_{max} 304 (ϵ 270), 328 (240) nm. Thus, **2** is synthesized from **7** in 90% yield. The cyclization of the dibromide **8** is less satisfactory, yielding **2** in only 60% yield. Compound **2** is rather air sensitive and is converted to the corresponding oxa compound **9**[5] on standing in air for several days at room temperature.

Scheme I



Synthesis of 2a. The synthetic methodology described above for **2** appears to be generally applicable. For example, hexaisopropylcyclotrisilane (**2a**) can be prepared in an equally satisfactory fashion. Treatment of a mixture of chlorodiisopropylsilane (**3a**) and dichlorodiisopropylsilane (**4a**) (1:0.34 molar ratio) with lithium (1.7 equiv) provides, in addition to 1,1,2,2-tetraisopropyldisilane (**6a**),[5] 1,1,2,2,3,3-hexaisopropyltrisilane (**5a**)[5] (40% yield), which in turn is chlorinated to yield the corresponding dichloro derivative (**7a**).[5] Reductive cyclization of **7a** under the conditions specified above successfully produces **2a**[5] in 85% yield (estimated by gas chromatography), which can be isolated virtually pure through the vacuum transfer technique. Compound **2a** is instantly converted to its (mono and di) oxa derivatives in contact with oxygen.[7]

Photolysis of 2. As compared with **1**[1] and a bridged compound **10**,[8] photoinduced fragmentation of **2** proceeds rather inefficiently.

(1) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150.
(2) For instance, the UV absorption of polysilanes and polygermanes is significantly affected by aryl substitution. See: Castel, A.; Rivière, P.; Saint-Roch, B.; Satgé, J.; Malrieu, J. P. *J. Organomet. Chem.* **1983**, *247*, 149.
(3) (a) Reaction of **4a** with Li leads to the corresponding cyclotetrasilane (Watanabe, H.; Muraoka, T.; Kageyama, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, C45). (b) $(t\text{-BuMeSi})_4$ is prepared from *tert*-butyldichloromethylsilane (Biernbaum, M.; West, R. *Ibid.* **1977**, *131*, 179).
(4) This reaction follows a standard procedure for the silicon chain extension. For instance, see: Gilman, H.; Harrell, R. L. *J. Organomet. Chem.* **1966**, *5*, 201.
(5) See supplementary material for spectral properties of this compound.
(6) The solvent ratio (1:8 of THF and pentane) is critical. With THF alone or without *t*-BuLi a considerable amount of **5** is produced as a byproduct which is difficult to separate from **2**. Use of naphthalene (catalytic amount) is also necessary. Naphthalene appears to effect smooth lithiation of the SiCl functionality.
(7) The air sensitivity of the strained Si–Si bond depends highly on its substituents. For the case of the cyclotetrasilane, see: (a) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51. (b) Hengge, E.; Schuster, H. G.; Peter, W. *J. Organomet. Chem.* **1980**, *186*, C45.

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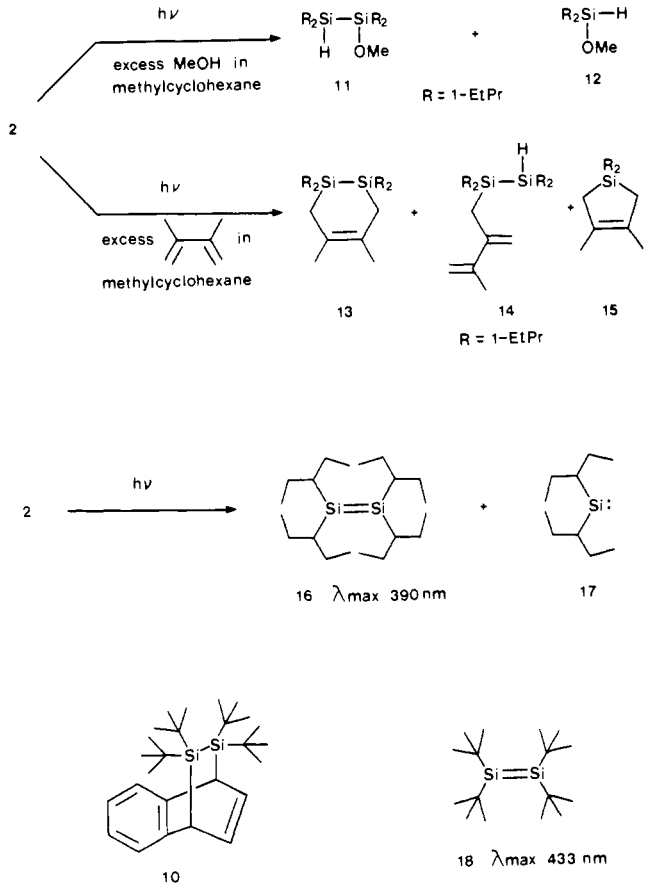
Scheme II



Thus, complete disappearance of **2** (60 mg in 4 mL of methylcyclohexane, 2×10^{-2} M) requires several hours of irradiation with a spiral low-pressure mercury lamp (125-watt output) at 4 °C. In the presence of methanol (1 M), this photolysis of **2** provides 1,1,2,2-tetrakis(1-ethylpropyl)methoxydisilane (**11**) (97% yield)[5] and bis(1-ethylpropyl)methoxysilane (**12**) (82%),[5] while the use of 2,3-dimethylbutadiene as a trapping agent leads to the formation of compounds **13**[5] (19% yield), **14**[5] (29%), and **15**[5] (56%) (see Scheme II). These experiments clearly demonstrate that the primary photoproducts are the disilene **16** and silylene **17**, as earlier observed for **1**.[1,8] In the absence of a trapping agent, the photolysate develops yellow coloration (λ_{max} at 390 nm) which is almost certainly ascribed to **16**, as the color disappears instantly upon addition of methanol. That this absorption appears at a wavelength shorter than that (433 nm) of tetra-*tert*-butyldisilene (**18**)[8] is of great interest.[9] We plan to present elsewhere an interpretation of this fact as well as an account of both the ground and excited states of alkylcyclotrisilanes, which are now readily available.[10]

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Supplementary Material Available: A listing of physical properties of new compounds (4 pages). Ordering information is given on any current masthead page.

(8) Masamune, S.; Murakami, S.; Tobita, H., unpublished results.
(9) Also note that tetrakis(2,6-dimethylphenyl)disilene has a UV absorption maximum at 422 nm. (a) Reference 1 and (b) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343.
(10) **Note Added in Proof**: After the submission of this communication a report on the synthesis of another cyclotrisilane appeared. Watanabe, H.; Okawa, T.; Kato, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 781.

Methods for Indole Alkaloid Synthesis: An Exceptionally Mild Procedure for Introducing the 6,7 Double Bond into Aspidosperma Alkaloids via Thiolactams†

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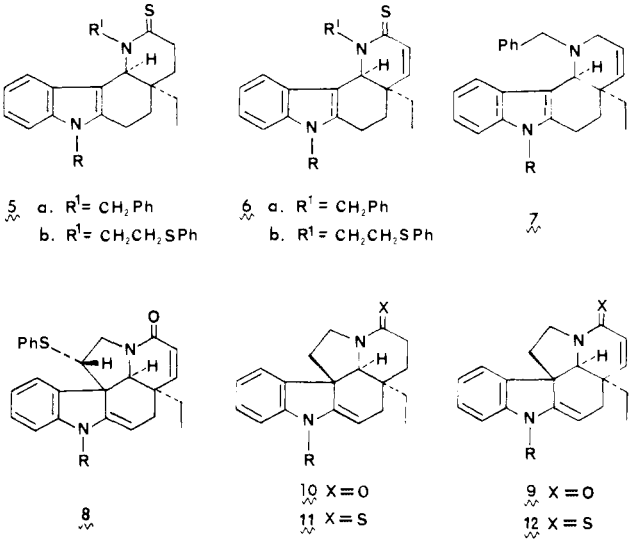
During recent years many new and versatile methods have been developed to introduce a double bond in conjugation with a carbonyl group. Only phenylselenylation of an amide enolate has been applied to the general problem of making the 6,7 double bond in Aspidosperma type alkaloids, but this procedure did not work for the systems described here.[1]

Here we describe a mild new method specifically designed to introduce the 6,7 double bond into alkaloid precursors (Scheme I). Such a transformation (**3** → **4**) is essential if the more highly functionalized indole alkaloids such as tabersonine or vindoline are to be synthesized by the indole-2,3-quinodimethane strategy.[2]

Treatment of the imine **1a** with the mixed carbonic anhydride **2**, (from 4-ethyl-4-pentenoic acid/Et_3N/vinyl chloroformate) in chlorobenzene at 140 °C for 18 h gave the tetracyclic lactam **3a** (50%; mp 204–205 °C).[2] Attempts to convert **3a** into the α,β-unsaturated amide **4a** using a variety of procedures (LDA/PhSeBr, LDA/$PhSO_2SPh$, $LiN(SiMe_3)_2/PhSO_2SPh$) only gave the starting lactam **3a** and intractable decomposition products.

Since protons adjacent to a thiolactam (ca. pK_a = 12–16) are considerably more acidic than those adjacent to a lactam (ca. pK_a = 32–36), we reasoned that a thiolactam should be readily dehydrogenated by treatment with a sulfinylating agent under mild conditions. Treatment of **3a** with the Lawesson reagent[3] (HMPA/85 °C/20 h) gave the thiolactam **5a** in 61% yield, (mp 201–202 °C). The thiolactam **5a** was treated with *p*-toluene-



sulfinyl chloride (CH_2Cl_2/N-*i*-Pr_2Et/0 °C/30 min) followed by aqueous acetic acid workup to give the α,β-unsaturated thiolactam **6a** in 75% yield (mp 221–225 °C). Subsequent desulfurization

† Dedicated to Professor Sir Derek Barton, on the occasion of his 65th birthday.

(1) Lévy, J.; Laronze, J.-Y.; Laronze, J.; LeMen, J. *Tetrahedron Lett.* **1978**, 1579. For syntheses of tabersonine that involve specific methods of introducing the C-6,C-7 double bond, see: Ziegler, F. E.; Bennett, G. B. *J. Am. Chem. Soc.* **1973**, *95*, 7458. Kutney, J. P.; Badger, R. A.; Beck, J. F.; Bosshardt, H.; Matough, F. S.; Ridaura-Sanz, V. E.; So, Y. H.; Sood, R. S.; Worth, B. R. *Can. J. Chem.* **1979**, *57*, 289. Ando, M.; Büchi, G.; Ohnuma, T. *J. Am. Chem. Soc.* **1975**, *97*, 6880.
(2) Gallagher, T.; Magnus, P. *J. Am. Chem. Soc.* **1982**, *104*, 1140; **1983**, *105*, 2086.
(3) Scheibye, S.; Pedersen, B. S.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 229.

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