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Hexamethylsilirane. 6. Conversion to 1-Oxa-2-silacyclopentanes by "Two-Atom" Insertion Reactions of Aldehydes and Ketones[1]

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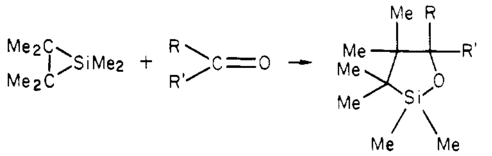
Activated aldehydes and ketones react with hexamethylsilirane at room temperature with insertion of the C=O bond into the SiC_2 ring to give 1-oxa-2-silacyclopentanes. Aliphatic aldehydes and ketones require UV irradiation for such insertion to occur. These reactions are rationalized in terms of molecule-induced homolysis of the silirane to give a 1,5-diradical intermediate, $RR'\dot{C}OSiMe_2CMe_2\dot{C}Me_2$. Examples of C=N and N=N bond insertion into hexamethylsilirane also are described.

Introduction

In part 5 of this series[1] we reported novel "two-atom" insertion reactions of aryl olefins, terminal 1,3-dienes, and terminal acetylenes with hexamethylsilirane, 1 (Scheme I). These reactions were rather unusual in the context of known silacarbocycle chemistry, and we wondered if other unsaturated substrates would undergo similar "two-atom" insertions into the highly reactive[2] silirane ring of 1. We report here our study of the reactions of hexamethylsilirane with aldehydes and ketones, an imine, and *trans*-azobenzene.

Results and Discussion

In the initial experiments, representative aldehydes and ketones were mixed with a THF solution of hexamethylsilirane under an argon atmosphere. In no case did an exothermic reaction occur. However, α,β-unsaturated aldehydes and ketones were found to react with the silirane *at room temperature* during an overnight reaction period. The products were 1-oxa-2-silacyclopentanes (2) as indicated in eq 1. Table I lists products and yields. The yields ranged from 50% in the case of crotonaldehyde to 100% in the case of the thiophene-derived carbonyl compounds. The reactions of hexamethylsilirane with biacetyl and acetylphenyldiimide demonstrate that functional substituents may be introduced into the 1-oxa-2-silacyclopentane ring system.



(1)

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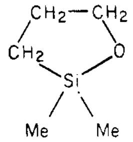
The parent 1-oxa-2-silacyclopentane 3 is known,[3] and it is a highly reactive compound. It polymerized readily at room temperature in the presence of even minute amounts of water to give a viscous liquid believed to be $HO[Me_2Si(CH_2)_3O]_nH$. Our products of type 2, on the other hand, appear to be quite stable toward traces of moisture. Undoubtedly, they are less reactive because they are so highly substituted.



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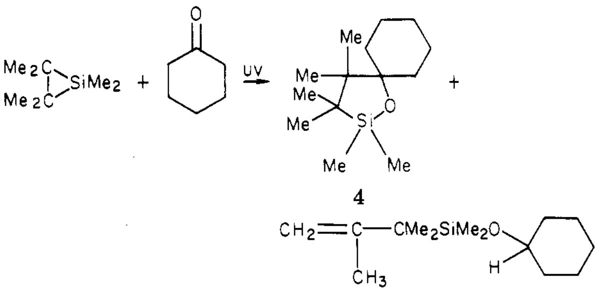
Saturated aldehydes and ketones (Me_3CCHO, C_2H_5CHO, Me_2CO, cyclohexanone) did not react with hexamethylsilirane under these conditions. When methanol was added to these reaction mixtures after they had been stirred overnight under argon at room temperature, an exothermic reaction produced the hexamethylsilirane methanolysis product, $Me_2CHCMe_2SiMe_2OMe$,[2b] in high yield, showing that the silirane had not reacted with the carbonyl compound.

However, when a pentane solution of propanal and hexamethylsilirane was irradiated with a 100-W UV lamp for 5 h, a 40% yield of 2 (R = Et, R′ = H) was obtained. Similar irradiation of a pentane solution containing the silirane and acetone resulted in a 34% yield of 2 (R = R′ = Me). Irradiation of a solution of 2,2-dimethylpropionaldehyde or cyclohexanone and hexamethylsilirane also gave the corresponding two-atom insertion products in low to moderate yield. In the cyclohexanone reaction a second, lower yield product (5) was obtained (eq 2). Thermolysis of hexamethylsilirane in the presence of cyclohexanone gave 4 in 7% yield, together with tetramethylethylene (74%). The presence of the latter is indicative of the decomposition of hexamethylsilirane with extrusion of Me_2Si,[4] but no product derived from reaction of the si-



(2)

5

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(1) (a) Part 5: Seyferth, D.; Duncan, D. P.; Shannon, M. L.; Goldman, E. W. *Organometallics*, preceding paper in this issue. (b) Preliminary communication: Seyferth, D.; Duncan, D. P.; Vick, S. C. *J. Organomet. Chem.* **1977**, *125*, C5. Seyferth, D.; Vick, S. C.; Shannon, M. L.; Lim, T. F. O.; Duncan, D. P. *Ibid.* **1977**, *135*, C37.

(2) (a) Seyferth, D.; Annarelli, D. C.; Shannon, M. L.; Escudie, J.; Duncan, D. P. *J. Organomet. Chem.* **1982**, *225*, 177. (b) Seyferth, D.; Annarelli, D. C.; Vick, S. C.; Duncan, D. P. *Ibid.* **1980**, *201*, 179. (c) Seyferth, D.; Duncan, D. P.; Haas, C. K. *Ibid.* **1970**, *164*, 305. (d) Seyferth, D.; Duncan, D. P.; Schmidbaur, H.; Holl, P. *Ibid.* **1978**, *159*, 137. (e) Hölderich, W.; Seyferth, D. *Ibid.* **1978**, *153*, 299.

(3) Speier, J. L.; David, M. P.; Eynon, B. A. *J. Org. Chem.* **1960**, *25*, 1637.

(4) (a) Seyferth, D.; Annarelli, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 7162. (b) Seyferth, D.; Annarelli, D. C.; Duncan, D. P. *Organometallics* **1982**, *1*, 1288.

0276-7333/84/2303-0579$01.50/0

Scheme I

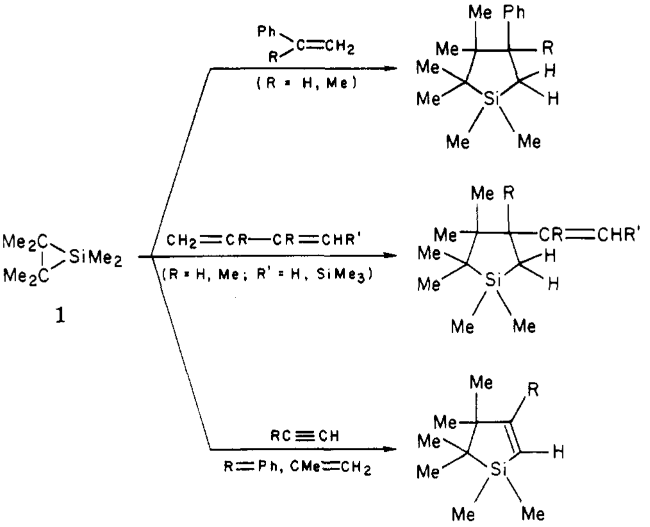
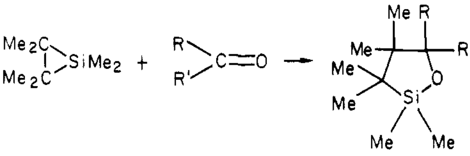
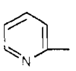
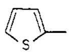
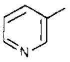
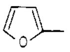
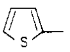
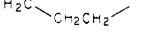


Table I. Reactions of Hexamethylsilirane with Aldehydes and Ketones

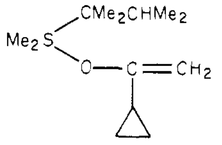


carbonyl compound		
R	R'	% yield of product
Ph	H	52
MeCH=CH	H	95
	H	65
	H	100
Me_3C	H	18[a]
C_2H_5	H	40[a]
Ph	CH_3	60
Ph	Ph	57
$Me_2C{=}CH$	CH_3	50
	CH_3	75
	CH_3	96
	CH_3	100
		57[a]
CH_3	CH_3	34[a]
$CH_3C({=}O)$	CH_3	95
$PhN{=}N$	CH_3	96

[a] Irradiation required.

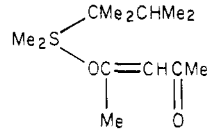
lylene with cyclohexanone was observed.[5]

Two ketones reacted anomalously, giving as sole products others than those derived from a two-atom insertion. Methyl cyclopropyl ketone was the only carbonyl compound among those examined which reacted exothermally with hexamethylsilirane. The product, which was obtained in 66% yield, was identified as 6 on the basis of its proton



6

NMR spectrum. In this case it would appear that the enol form of the ketone reacted with the silirane with Si–C bond heterolysis as had been observed previously with saturated alcohols and with phenol.[2a] Acetylacetone also reacted as an enol with hexamethylsilirane at room temperature, giving 7 in 89% yield.



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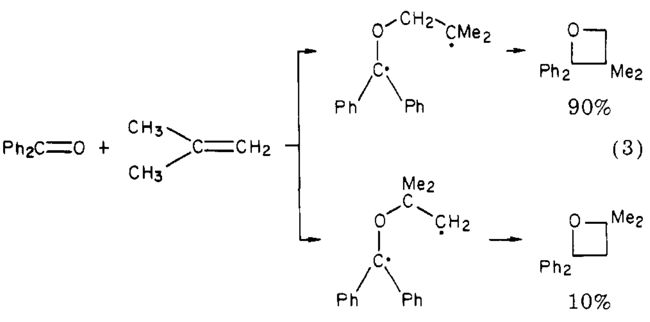
The mechanism of the $C{=}O$ insertion reactions into the Si—C bond of hexamethylsilirane was of interest to us. The most reactive carbonyl compounds in this two-atom insertion reaction are those which bear substituents that are capable of stabilizing an adjacent radical center (e.g., phenyl and vinylic substituents). Such resonance stabilization of an adjacent radical is not possible in aliphatic aldehydes and ketones, and their reactions with hexamethylsilirane required external excitation. Separate experiments showed that hexamethylsilirane is unaffected by irradiation with a 100-W UV lamp (quartz flask, pentane solution) at room temperature (3-h reaction time). It is thus reasonable to suggest that the active species in the two-atom insertion reactions is the excited state of the carbonyl compound, the n,π^* triplet state. Since this excited state is much less accessible in the case of aliphatic carbonyl compounds, irradiation is required for a reaction to occur.

One may view these reactions as mechanistically akin to the formation of oxetanes by cycloaddition of carbonyl compounds to simple alkenes, dienes, and acetylenes upon irradiation,[6] a reaction which may proceed via an initial exiplex and then a diradical derived from the latter.[6] It is proposed that in such reactions the diradical results from attack on the alkene by the electron-deficient oxygen atom of the excited $C{=}O$ group and that the more energetically stable of the two possible diradicals is formed more readily. Equation 3 shows one such reaction. Many examples of such "molecule-induced homolysis" are known.[7]



In the reaction of an aldehyde or a ketone in the excited n,π^* triplet state with hexamethylsilirane we would expect

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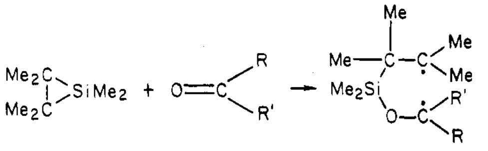
(5) The reactions of silylenes with enolizable ketones, $(RCH_2)_2CO$, give silyl enol ethers, $RCH_2C(OSiMe_2H){=}CHR$: (a) Ando, W.; Ikeno, M.; Sekiguchi, A. *J. Am. Chem. Soc.* 1977, *99*, 6447; 1978, *100*, 3613. (b) Ishikawa, M.; Nakagawa, K.; Kumada, M. *J. Organomet. Chem.* 1977, *135*, C45.

(6) Bartrop, J. A.; Coyle, J. D. "Excited States in Organic Chemistry"; Wiley: New York, 1975; pp 208–212.

(7) Pryor, W. A. "Free Radicals"; McGraw-Hill: New York, 1966; pp 119–124.

attack by the oxygen atom of the excited C=O group at silicon to form the thermodynamically very stable Si—O bond, i.e., radical 8 would be the intermediate (eq 4).



(4)

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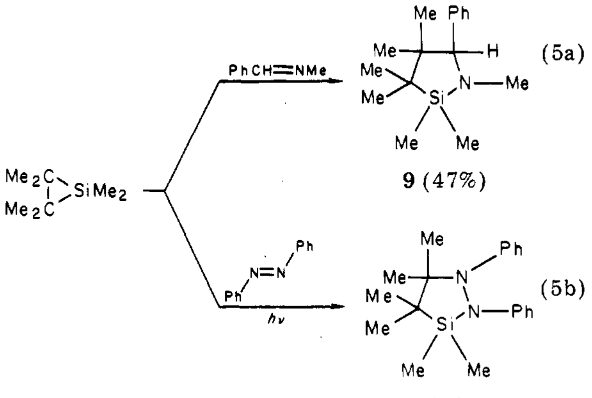
Closure of diradical 8 to give the five-membered ring product, the 1-oxa-2-silacyclopentane 2, would then be a very favorable process. Alternatively, hydrogen atom transfer reactions in 8 also would be a possibility, and the acyclic products obtained in the reactions of hexamethylsilirane with cyclohexanone, methyl cyclopropyl ketone, and acetylacetone could have been formed by such a process (but not necessarily so, since alternate mechanisms are possible). Although appropriate mechanistic studies remain to be done, we feel that a molecule-induced homolysis of hexamethylsilirane by the carbonyl compound which proceeds to products by way of diradicals of type 8 is a reasonable and likely explanation of these novel two-atom insertion reactions of hexamethylsilirane.

In conclusion, we note that compounds containing C=N and N=N bonds also can undergo two-atom insertion into hexamethylsilirane. Thus, benzaldehyde *N*-methylimine reacted with hexamethylsilirane at room temperature as shown in eq 5a, while *trans*-azobenzene required irradiation (Pyrex flask) to effect insertion in only modest yield.



(5a)

9 (47%)

(5b)

10 (28%)

Experimental Section

General Comments. Infrared spectra were recorded on a Perkin-Elmer Model 457A infrared spectrophotometer, proton magnetic resonance spectra on either a Varian Associates T60, a Perkin-Elmer R-20, or a Perkin-Elmer R-22 spectrometer. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Chloroform and dichloromethane often were used as alternative internal standards. ^{13}C NMR spectra were obtained with a Jeol FNM HFX-60Q spectrometer. Gas-liquid chromatography (GLC) was used routinely for isolation of pure samples, for determination of purity of distilled samples, and for yield determinations by the internal standard method. All columns were packed on acid-washed, dimethyldichlorosilane-treated Chromosorb W.

All solvents used were rigorously dried. All reactions were carried out under an atmosphere of prepurified nitrogen or argon. All glassware was flame dried under a stream of nitrogen before use. Reactive reagents were transferred by syringe or cannula.

In part 1[2b] the preparations of hexamethylsilirane and its precursors are described in detail, as are the methods used for the determination of the yield of hexamethylsilirane, for the preparation of solutions of hexamethylsilirane in solvents other than THF, and for the handling of hexamethylsilirane and its solutions. We stress again the high reactivity of hexamethylsilirane toward atmospheric oxygen and moisture and the absolute need to perform all operations involving this compound with complete exclusion of air in rigorously dried glassware using dried and degassed solvents.

The products of the reactions reported here were characterized by C/H analysis, IR and proton NMR spectroscopy, and, in some cases, mass spectroscopy. The IR spectra are listed in the M.I.T. Ph.D. theses of D. P. Duncan and M. L. Shannon and are not given here. The aldehyde and ketone two-atom insertion products into hexamethylsilirane all showed strong bands in the 1080–1000-cm^{-1} and 850–830-cm^{-1} regions in their IR spectra, which is indicative of an Si–O–C unit.[8]

Room Temperature Reactions of Hexamethylsilirane with Aldehydes and Ketones. All reactions were carried out in 50-mL three-necked flasks equipped with a no-air stopper, an argon inlet tube, and a magnetic stir bar. The reaction flask was purged with argon and flame-dried before addition of any reagents. After the flask had cooled, a weighed amount of hexamethylsilirane solution (in THF unless otherwise noted) of a known concentration was added by syringe, followed by a weighed amount of the appropriate liquid carbonyl compound. In those cases where the carbonyl compound was a solid, it was added to the reaction flask first, and then the silirane solution was added. After they had been stirred under argon at room temperature overnight, the reaction mixtures were weighed and analyzed by GLC. Generally nonpolar liquid phases (10% UC-W98, 10% or 20% SE-30, 10% DC-710, 10% DC-200) on Chromosorb W were used. Yields were determined by GLC using the internal standard method, and pure samples of the products were isolated by GLC for determination of the refractive index, for elemental analysis, and for spectroscopic measurements. Details of product characterization follow below.

Benzaldehyde (2.8 mmol) reacted with hexamethylsilirane (0.60 mmol) to give 2 (R = Ph; R' = H), $n^{25}{}_{D}$ 1.5103, in 52% yield. Anal. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74. Found: C, 72.57; H, 9.75. ^{1}H NMR (CCl_4) δ 0.18, 0.33 (s, 3 H each, CH_3Si), 0.53, 0.76, 0.94, 1.04 (s, 3 H each, CCH_3), 4.71 (s, 1 H, *H*-CPh), 7.18 (s, 5 H, Ph).

Crotonaldehyde (5 mmol) reacted with hexamethylsilirane (4.38 mmol) to give 2 (R = CH_3CH=CH; R' = H), $n^{25}{}_{D}$ 1.4641, in 95% yield. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.85; H, 11.39. Found: C, 68.05; H, 11.42. ^{1}H NMR (CCl_4) δ 0.05, 0.15 (s, 3 H each, CH_3Si), 0.66, 0.72 (s, 3 H each, CCH_3), 0.87 (s, 6 H, CCH_3), 1.70 (d, *J* = 4 Hz, 3 H, =CHC*H*$_3$), 3.96 (d, *J* = 5 Hz, 1 H, C*H*—CH=C), 5.36–5.60 (m, 2 H, vinyl H).

Pyridine-2-carboxaldehyde (4.0 mmol) reacted with hexamethylsilirane (1.49 mmol, in 15 mL of pentane) to give 2 (R = 2-pyridyl; R' = H), $n^{25}{}_{D}$ 1.5094, in 65% yield. Anal. Calcd for $C_{14}H_{23}ONSi$: C, 67.42; H, 9.29. Found: C, 67.48; H, 9.34. ^{1}H NMR (CCl_4) δ 0.22, 0.35 (s, 3 H each, $SiCH_3$), 0.52 (s, 3 H, CCH_3), 0.93 (s, 6 H, CCH_3), 1.09 (s, 3 H, CCH_3), 4.78 (s, 1 H, OC*H*), 6.9–7.6 (m, 3 H, β- and γ-pyridyl H), 8.3–8.5 (m, 1 H, α-pyridyl H).

Thiophene-2-carboxaldehyde (5 mmol in 1 mL of benzene) reacted with hexamethylsilirane (2.31 mmol in 10 mL of pentane) to give 2 (R = 2-thienyl; R' = H), $n^{25}{}_{D}$ 1.5163, in quantitative yield. Anal. Calcd for $C_{13}H_{22}OSSi$: C, 61.36; H, 8.71. Found: C, 61.62; H, 8.76. ^{1}H NMR (CCl_4) δ 0.16, 0.22 (s, 3 H each, $SiCH_3$), 0.65, 0.87, 0.96, 1.02 (s, 3 H each, CCH_3), 4.99 (s, 1 H, OC*H*), 6.75–6.97 (m, 2 H, β-thienyl H), 7.09–7.02 (m, 1 H, α-thienyl H).

Acetophenone (3 mmol) reacted with hexamethylsilirane (2.76 mmol) to give 2 (R = Ph; R' = CH_3), $n^{25}{}_{D}$ 1.5158, in 60% yield. Anal. Calcd for $C_{16}H_{26}OSi$: C, 73.22; H, 9.99. Found: C, 73.05; H, 9.97. ^{1}H NMR (CCl_4) δ 0.25, 0.29 (s, 3 H each, $SiCH_3$), 0.40, 0.84, 0.99, 1.14 (s, 3 H each, CCH_3), 1.54 (s, 3 H, C*H*$_3$CPh), 7.18 (s, 5 H, Ph).

Benzophenone (3 mmol) reacted with hexamethylsilirane (2.79 mmol) to give 2 (R = R' = Ph), mp 32 °C (GLC sample), in 57% yield. Anal. Calcd for $C_{21}H_{28}OSi$: C, 77.72; H, 8.70. Found: C, 77.61; H, 8.84. ^{1}H NMR (CCl_4) δ 0.29 (s, 6 H, $SiCH_3$), 0.70 (s, 6 H, CCH_3), 1.05 (s, 6 H, CCH_3), 6.9–7.2, 7.6–7.8 (m, 10 H, Ph).

Mesityl oxide (3 mmol) reacted with hexamethylsilirane (2.76 mmol) to give 2 (R = Me_2C=CH; R' = CH_3), $n^{25}{}_{D}$ 1.4688, in 50% yield. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.92; H, 11.75. Found:

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(8) Smith, A. L. *Spectrochim. Acta* **1960**, *16*, 87.

C, 69.75; H, 11.67. ^{1}H NMR (CCl_4) δ 0.06, 0.15 (s, 3 H each, $SiCH_3$), 0.86 (s, 6 H, CCH_3), 0.93, 0.97 (s, 3 H each, CCH_3), 1.21 (s, 3 H, $C\mathit{H}_3C{-}C{=}C$), 1.26 (d, *J* = 1.8 Hz, 3 H, $CH{=}CC\mathit{H}_3$), 1.82 (d, *J* = 1.8 Hz, 3 H, $CH{=}CC\mathit{H}_3$), 5.40 (broad s, 1 H, vinyl H).

3-Acetylpyridine (4.0 mmol) reacted with hexamethylsilirane (1.50 mmol in 15 mL of pentane) to give **2** (R = 3-pyridyl; R′ = CH_3), $n^{25}{}_D$ 1.5160, in 75% yield. Anal. Calcd for $C_{15}H_{25}ONSi$: C, 68.39; H, 9.56. Found: C, 68.45; H, 9.52. ^{1}H NMR (CCl_4) δ 0.20, 0.25 (s, 3 H each, $SiCH_3$), 0.38, 0.80, 0.95, 1.10 (s, 3 H each, CCH_3), 1.52 (s, 3 H, O-C-CH_3), 6.9–7.3 (m, 1 H, β-pyridyl H), 7.4–7.7 (m, 1 H, γ-pyridyl H), 8.2–9.6 (m, 2 H, α-pyridyl H).

2-Acetylfuran (4 mmol) reacted with hexamethylsilirane (1.69 mmol in 15 mL of pentane) to give **2** (R = 2-furyl; R′ = CH_3), $n^{25}{}_D$ 1.4872, in 96% yield. Anal. Calcd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58. Found: C, 66.66; H, 9.58. ^{1}H NMR (CCl_4) δ 0.17, 0.21 (s, 3 H each, $SiCH_3$), 0.64, 0.74, 1.00, 1.01 (s, 3 H each, CCH_3), 1.43 (s, 3 H, O-C-CH_3), 6.00–6.22 (m, 2 H, β-furyl H), 7.20 (m, 1 H, α-furyl H).

2-Acetylthiophene (5 mmol) reacted with 2.22 mmol of hexamethylsilirane in 15 mL of pentane to give **2** (R = 2-thienyl; R′ = CH_3), $n^{25}{}_D$ 1.5177, in quantitative yield. Anal. Calcd for $C_{14}H_{24}OSSi$: C, 62.63; H, 9.01. Found: C, 62.65; H, 8.96. ^{1}H NMR (CCl_4) δ 0.22, 0.28 (s, 3 H each, $SiCH_3$), 0.64, 0.86, 1.01, 1.12 (s, 3 H each, CCH_3), 1.46 (s, 3 H, O-C-CH_3), 6.67–6.91 (m, 2 H, β-thienyl H), 6.97–7.06 (m, 1 H, α-thienyl H).

2,3-Butanedione (4 mmol) reacted with hexamethylsilirane (1.60 mmol in 15 mL of pentane) to give **2** (R = C(O)CH_3; R′ = CH_3), mp 39–40 °C (GLC sample), in 95% yield. Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 63.10; H, 10.63. ^{1}H NMR (CCl_4) δ 0.15, 0.21 (s, 3 H each, $SiCH_3$), 0.79, 0.85, 0.91, 1.04 (s, 3 H each, CCH_3), 1.21 (s, 3 H, O-C-CH_3), 2.09 (s, 3 H, $O{=}C{-}CH_3$).

Acetylphenyldiimide, $CH_3C(O)N{=}NPh$ (10 mmol), reacted with hexamethylsilirane (9.4 mmol) to give **2** (R = PhN═N; R′ = CH_3), $n^{25}{}_D$ 1.5308, in 96% yield. Anal. Calcd for $C_{16}H_{26}N_2OSi$: C, 66.16; H, 9.02. Found: C, 65.96; H, 8.87. ^{1}H NMR (CS_2/dioxane): δ 0.23, 0.28 (s, 3 H each, $SiCH_3$), 0.72, 0.79, 0.95, 1.05 (s, 3 H each, CCH_3), 1.27 (s, 3H, O-C-CH_3), 7.25–7.60 (m, 5 H, Ph).

Cyclopropyl methyl ketone (26.7 mmol) reacted with hexamethylsilirane (5.10 mmol) in an exothermic reaction (1 h) to give dimethyl(2,3-dimethyl-2-butyl)silyl 1-cyclopropylvinyl ether (**6**), $n^{25}{}_D$ 1.4639, in 66% yield. Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.95; H, 11.57. Found: C, 68.92; H, 11.57. ^{1}H NMR (CCl_4) δ 0.21 (s, 6 H, $SiMe_2$), 0.88 (s, 6 H, CMe_2), 0.89 (d, *J* = 7.5 Hz, 6 H, $CH(C\mathit{H}_3)_2$), 0.36–1.99 (complex m, 6 H, cyclopropyl H and $C\mathit{H}Me_2$), 3.88, 4.02 (broad s, 2 H, vinyl H). The 70-eV mass spectrum showed the molecular ion, M^+, at *m/z* 226.

Acetylacetone (19.57 mmol) reacted with hexamethylsilirane (4.24 mmol) to give **7**, $n^{25}{}_D$ 1.4731, in 89% yield. Anal. Calcd for $C_{13}H_{26}O_2Si$: C, 64.40; H, 10.81. Found: C, 64.33; H, 10.76. ^{1}H NMR (CCl_4) δ 0.29 (s, 6 H, $SiCH_3$), 0.93 (s, 6 H, CMe_2), 0.95 (d, *J* = 6.6 Hz, 6 H, $CH(C\mathit{H}_3)_2$), 1.24–1.59 (septet, *J* = 6.6 Hz, 1 H, $C\mathit{H}(CH_3)_2$), 2.04 (s, 3 H, $O{=}CCH_3$), 2.29 (s, 3 H, $C\mathit{H}_3C(O){-}$), 5.46 (s, 1 H, $O{-}C{=}CHC{=}O$).

Photochemically Induced Reactions of Hexamethylsilirane with Aldehydes and Ketones. 2,2-Dimethylpropionaldehyde. A solution of 0.923 g of hexamethylsilirane (THF concentrate, 2.58 mmol) and 0.544 mL (5 mmol) of Me_3CCHO in 15 mL of pentane was irradiated for 4.5 h in an argon-purged one-necked quartz flask equipped with a magnetic stir bar and a reflux condenser topped with an argon inlet tube. The irradiation was effected with a Hanovia UV quartz lamp (Type 30620) at a distance of 4 cm from the reaction flask (henceforth "standard irradiation conditions"). Subsequent GLC analysis showed the presence of **2** (R = Me_3C; R′ = H), $n^{25}{}_D$ 1.4566, in 18% yield. Anal. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35. Found: C, 68.10; H, 12.15. ^{1}H NMR (CCl_4) δ 0.11, 0.20 (s, 3 H each, $SiCH_3$), 0.83, 0.88, 0.91, 0.96 (s, 3 H, CCH_3), 1.03 (s, 9 H, CMe_3), and 3.32 (s, 1 H, O-C-H).

A control experiment carried out without irradiation (9.2 mmol of Me_3CCHO; 1.93 mmol of the silirane) at room temperature overnight gave no two-atom insertion product (GLC analysis of an aliquot). Addition of methanol to the reaction mixture resulted in an exothermic reaction which produced $Me_2CHCMe_2SiMe_2OMe$ in 91% yield.

Propanal (12 mmol) reacted with hexamethylsilirane (4.87 mmol in 15 mL of pentane) under standard irradiation conditions to give **2** (R = C_2H_5; R′ = H), $n^{25}{}_D$ 1.4488, in 21% yield. Anal. Calcd. for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07. Found: C, 65.58; H, 12.01. ^{1}H NMR (CCl_4) δ 0.03, 0.11 (s, 3 H each, $SiCH_3$), 0.67, 0.74 (s, 3 H each, CCH_3), 0.84 (s, 6 H, CCH_3), 0.96 (t, *J* = 6.0 Hz, 3 H, $C\mathit{H}_3$ of Et), 1.07–1.45 (m, 2 H, CH_2 of Et), and 3.42 (t, *J* = 5.5 Hz, 1 H, O-C-H).

No reaction took place in the absence of irradiation.

Acetone (5 mmol) reacted with hexamethylsilirane (2.84 mmol in 15 mL of pentane) under standard irradiation conditions to give **2** (R = R′ = CH_3), $n^{25}{}_D$ 1.4551, in 34% yield. Anal. Calcd for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07. Found: C, 65.65; H, 12.23. ^{1}H NMR (CCl_4) δ 0.16 (s, 6 H, $SiMe_2$), 0.86, 1.02, 1.20 (s, 6 H each, CMe_2).

No reaction occurred in the absence of irradiation.

Cyclohexanone (5 mmol) reacted with hexamethylsilirane (2.76 mmol in 15 mL of pentane) under standard irradiation conditions to give **4**, $n^{25}{}_D$ 1.4829, in 57% yield. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 69.90; H, 11.80. ^{1}H NMR (CCl_4) δ 0.10 (s, 6 H, Me_2Si), 0.79, 0.97 (s, 6 H each, Me_2C), 1.02–1.85 (m, 10 H, $(CH_2)_5$).

A minor, more volatile product (**5**), $n^{25}{}_D$ 1.4647, also was present in 14% yield. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 69.75; H, 11.64. Mass spectrum (70eV), M^+ at *m/z* 240. ^{1}H NMR (CCl_4) δ 0.01 (s, 6 H, $SiMe_2$), 1.07 (s, 6 H, CMe_2), 1.1–1.5 (m, 10 H, $(CH_2)_5$), 1.80 (s, 3 H, $CH_3C{=}$), 3.68 (m, 1 H, $O{-}C{-}H$), 4.6 (m, 2H, $={CH_2}$).

No reaction occurred at room temperature in the absence of irradiation. However, a reaction carried out between 1.72 mmol of hexamethylsilirane and neat cyclohexanone at 70 °C for 18 h under argon gave the two-atom insertion product **4** (7% yield), as well as a 74% yield of tetramethylethylene.

Reaction of Hexamethylsilirane with Benzaldehyde *N*-Methylimine. To 9.2 g of a THF solution containing 4.33 mmol of hexamethylsilirane (under argon) was added 5 mmol of $PhCH{=}NCH_3$ (Aldrich). The reaction mixture became yellow when the reactants were mixed. It was stirred at room temperature overnight. Subsequent GLC analysis (10% DC-200, 190 °C) showed the presence of one major product, 1,1,2,2,3,3,5-heptamethyl-4-phenyl-5-aza-1-silacyclopentane (**9**), a liquid, $n^{25}{}_D$ 1.5180, in 47% yield. Anal. Calcd for $C_{16}H_{27}NSi$: C, 73.49; H, 10.41. Found: C, 73.52; H, 10.38. ^{1}H NMR (C_6D_6) δ 0.15, 0.32 (s, 3 H each, $SiCH_3$), 0.80, 0.84, 0.97, 0.99 (s, 3 H each, CCH_3), 2.31 (s, 3 H, CH_3N), 3.86 (s, 1 H, *H*-CPh), and 7.31 (m, 5 H, Ph).

Reaction of Hexamethylsilirane with *trans*-Azobenzene. A flame-dried 100-mL one-necked Pyrex flask equipped with a magnetic stir bar and a reflux condenser topped with an argon inlet tube was charged with a solution of 3.50 g (19.2 mmol) of *trans*-azobenzene and 0.6418 g of a 3.54 mmol/g solution of hexamethylsilirane (2.27 mmol) in 10 mL of pentane. The solution was irradiated with a 100-W mercury vapor UV lamp for 2 h at room temperature. Subsequent GLC analysis (10% SE-30, 90–220 °C program) showed the presence of 2,3-diphenyl-1,1,4,4,5,5-hexamethyl-2,3-diaza-1-silacyclopentane (**10**) in 28% yield. The product was collected by GLC as a viscous yellow gum. Anal. Calcd for $C_{20}H_{28}N_2Si$: C, 74.01; H, 8.70; N, 8.63. Found: C, 73.73; H, 8.66; N, 8.21. ^{1}H NMR (CCl_4) δ 0.50 (s, 6 H, $SiMe_2$), 0.90, 1.29 (s, 6 H each, CMe_2), 6.36–7.73 (m, 10 H, Ph).

Experiments in which the irradiation was carried out in a quartz flask gave only a 7% yield of **10** when a pentane solution of the reactants was irradiated and a 17% yield when a benzene solution was irradiated.

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Registry No. 1, 55644-09-2; **2** (R = Ph; R′ = H), 88780-38-5; **2** (R = MeCH═CH; R′ = H), 62346-54-7; **2** (R = 2-pyridyl; R′ = H), 88780-39-6; **2** (R = 2-thienyl; R′ = H), 88780-40-9; **2** (R = Me_3C; R′ = H), 88780-48-7; **2** (R = C_2H_5; R′ = H), 64588-35-8; **2** (R = Ph; R′ = CH_3), 62386-03-2; **2** (R = R′ = Ph), 88780-41-0; **2** (R = $Me_2C{=}CH$; R′ = CH_3), 88780-42-1; **2** (R = 3-pyridyl; R′ = CH_3), 88780-43-2; **2** (R = 2-furyl; R′ = CH_3), 88780-44-3; **2** (R = 2-thienyl; R′ = CH_3), 88780-45-4; **2** (R = ClO)CH_3; R′ = CH_3), 88780-46-5; **2** (R = PhN=N; R′ = CH_3), 88780-47-6; **2** (R = R′ = CH_3), 64588-23-4; **4**, 88780-49-8; **5**, 88780-50-1; **6**, 88780-51-2; **7**, 88780-52-3; **9**, 62346-57-0; **10**, 88780-53-4; $CH_3C(O)N$=NPh, 13443-97-5; PhCH=NCH_3, 622-29-7; benzaldehyde, 100-52-7; crotonaldehyde, 4170-30-3; pyridine-2-carboxaldehyde, 1121-60-4; thiophene-2-carboxaldehyde, 98-03-3; acetophenone, 98-86-2; benzophenone, 119-61-9; mesityl oxide, 141-79-7; 3-acetylpyridine, 350-03-8; 2-acetylfuran, 1192-62-7; 2-acetylthiophene, 88-15-3; 2,3-butanedione, 431-03-8; cyclopropyl methyl ketone, 765-43-5; acetylacetone, 123-54-6; 2,2-dimethylpropionaldehyde, 630-19-3; propanal, 123-38-6; acetone, 67-64-1; cyclohexanone, 108-94-1; *trans*-azobenzene, 17082-12-1.

Theoretical Studies of Cyclic $C_2Si_2H_4$ Molecules

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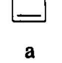
Thirteen cyclic $C_2Si_2H_4$ isomers, including disilatetrahedrane and the disilacyclobutadienes, have been studied by using ab initio quantum mechanics. At the MP3/6-31G*//3-21G level of computation, the silyl-substituted silacyclopropenylidene is found to be the most stable. Disilatetrahedrane is quite high on the energy surface, and the two possible planar 1,2-disilacyclobutadienes do not represent minima on this surface. Planar 1,3-disilacyclobutadiene is a stable structure and exhibits significant diradical character.

Introduction

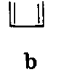
Compounds containing highly strained carbon rings have been of interest to experimental[1] and theoretical[2] chemists for some time. In particular, much interest has centered around the elusive cyclobutadiene and tetrahedrane molecules.[3] Investigation of silicon-containing analogues to these small carbon rings, however, has hardly begun. For the case of four-membered rings, only single substitutions have been investigated to date.[4] In that paper, silatetrahedrane was found to be much less stable than silacyclobuta-1,3-diene but more stable than its dissociation products. The study of ring systems with two carbon atoms replaced by silicons is the next logical extension of this work.

The $C_2Si_2H_4$ system is of particular interest because of the variety of bonding situations that may be hypothesized for silicon. These include single bonds to silicon, double bonds to silicon, and double bonds to carbon. Since these bonds occur within one system, a direct comparison of relative bond strengths may be made. The $C_2Si_2H_4$ system is also the simplest prototype for important structures in synthetic organosilicon chemistry. The basic ring structures of the normal valent compounds provide fundamental understanding useful in developing successful synthetic routes to these highly reactive species. The investigation of these prototypes was the primary motivation for the present work.

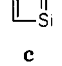
Since cyclobutadiene analogues are four π electron "antiaromatic" species, one can imagine three formal localized structures:



a



b



c

If these structures correspond to stable minima, they provide an interesting comparison of C=C vs. C=Si vs. Si=Si double bonds. In addition, **c** may exhibit significant diradical behavior. Beyond isomers **a**, **b**, and **c** and disilatetrahedrane, several other cyclic $C_2Si_2H_4$ species, especially those containing silylene functional groups, are of interest. The latter structures allow for the comparison of silicon-containing multiple bonds with silylenes. Characterized structures and corresponding energies are presented in the current work. Investigation of acyclic isomers will be presented in a future paper.

Methodology

All isomers characterized were optimized by using the Schlegel method[5] and the GAUSSIAN80 program package,[6] with the 3-21G basis set.[7] Single point energy calculations were carried out at the 3-21G optimal geometries using the extended 6-31G* basis set.[8] Correlation was accounted for with use of third-order Møller–Plesset perturbation theory (MP3).[9] Because of the size of the molecules studied, correlation corrections and basis set corrections, i.e., polarization functions, are assumed to be additive in order to obtain MP3/6-31G* relative stabilities. This assumption offers a considerable savings in computer time, especially in large systems, while giving results to within 4–5 kcal/mol of an actual calculation.[10]

Diradical behavior was investigated by using π space UHF-NO CI[11] and FORS MCSCF[12] wave functions, containing the 12 $^1A_1$ configurations obtained by distributing the four π electrons among the four π orbitals in all pos-

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[1] (a) Lin, C. Y.; Krantz, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1111. (b) Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.*, **1973**, *95*, 615. (c) Maier, G.; Pfreim, S.; Schafer, U.; Matusch, R. *Angew. Chem.* **1978**, *90*, 552.

[2] (a) Buenker, R. J.; Peyerimhoff, S. D. *J. Am. Chem. Soc.* **1969**, *91*, 4342. (b) Schulman, J. M.; Venanzi, T. J. *Ibid.* **1974**, *96*, 4739. (c) Hehre, W. J.; Pople, J. A. *Ibid.* **1975**, *97*, 6941.

[3] (a) Newton, M. D. In "Applications of Electronic Structure Theory"; Schaefer, H. F. Ed.; Plenum Press: New York, 1977; pp 223–275. (b) Kollmar, H. *J. Am. Chem. Soc.* **1980**, *102*, 2617.

[4] Gordon, M. S. *J. Chem. Soc., Chem. Commun.* **1980**, 1131.

[5] Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

[6] Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, J.; Kuhn, L. R.; Pople, J. A. *QCPE* **1980**, *13*, 406.

[7] Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J. *Ibid.* **1982**, *104*, 2797.

[8] Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

[9] Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quantum Chem.* **1979**, *S11*, 149.

[10] Gordon, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 4352. McKee, M. L.; Lipscomb, W. N. *Ibid.* **1981**, *103*, 4623.

[11] Yamaguchi, K.; Ohta, K.; Yabushita, S.; Fueno, T. *Chem. Phys. Lett.* **1977**, *49*, 555.

[12] Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M.; Elbert, S. T. *Chem. Phys.* **1982**, *71*, 48.

0276-7333/84/2303-0583$01.50/0