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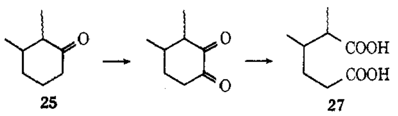

25 **27**

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Unsaturated Organosilicon Heterocycles

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The photolytic addition of H_2S to dimethyldiallylsilane yields 1,1-dimethyl-1-sila-5-thiacyclooctane. Oxidation of the sulfide yields the corresponding sulfone, which can be directly converted *via* a modified Ramberg–Backlund reaction into 1,1-dimethyl-1-sila-4-cycloheptene. This reaction sequence has also been used to prepare 1,1-diphenyl-1-sila-4-cycloheptene from diphenyldiallylsilane. An alternate synthesis of 1,1-dimethyl-1-sila-4-cycloheptene and 1,1-diphenyl-1-sila-4-cycloheptene is also reported.

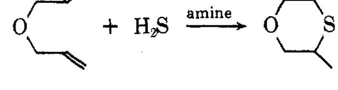
We have been concerned with improving synthetic routes to seven- and eight-membered organosilicon heterocycles.[1] The modified acyloin reaction[2,3] on suitable organosilicon diesters has been the best entry into these ring systems. For instance, dimethyl 4,4-dimethyl-4-sila-1,7-heptanedioate can be cyclized to 1,1-dimethyl-4,5-bis(trimethylsiloxy)-1-sila-4-cycloheptene in good yield.[1] However, two problems remain. One is that the synthesis of suitable organosilicon diester substrates for the acyloin reaction often involves many steps from commercially available dichlorosilanes. The second is that the heterocycle formed after hydrolysis of the trimethylsilyl ether protecting groups contains an α-hydroxy ketone functionality which requires several steps to transform into a carbon–carbon double bond. To solve these problems we have developed a new synthetic entry into these heterocyclic systems.

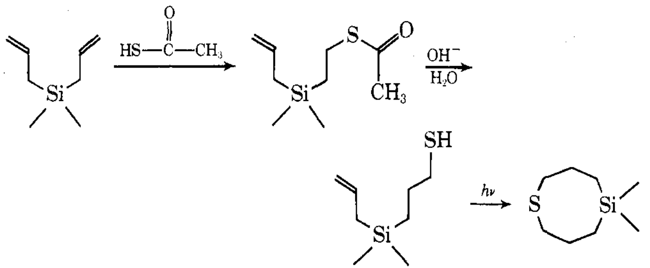
There are several recent examples of the use of organosulfur compounds to establish both carbon–carbon single[4,5] and carbon–carbon double bonds. The conversion of a sulfide to a carbon–carbon double bond by a double Stevens rearrangement is one example from the latter category.[6,7] The Ramberg–Backlund reaction, which converts an α-chloro sulfone into an alkene, is another.[8-12]

We decided to attempt to prepare cyclic compounds containing silicon and sulfur by addition of H_2S to dimethyldiallylsilane and to diphenyldiallylsilane owing to the ready availability of these organosilicon compounds.[1,13] We find that H_2S adds to dimethyldiallylsilane in a dilute pentane solution at −78° upon irradiation through a quartz photolysis well with a 450-W medium-pressure Hanovia lamp to form 1,1-dimethyl-1-sila-5-thiacyclooctane in 25% isolated yield.[14] Similarly, H_2S adds to diphenyldiallylsilane upon irradiation at −78° to form 1,1-diphenyl-1-sila-5-thiacyclooctane in 10% isolated yield.

This is remarkable considering the problems involved in synthesis of medium-sized ring compounds from alicyclic precursors. For instance, closure of ω-chloro sulfides $RS(CH_2)_nCl$ to form cyclic sulfonium salts fails for n = 6–11.[15] The fact that both C–Si (1.87 Å) and C–S (1.82 Å) bonds are longer than C–C single bonds may make formation of 1,1-dimethyl-1-sila-5-thiacyclooctane more like cyclization of a nine-membered than an eight-membered all-carbon ring system.[16] Ring closure reactions are usually most difficult to accomplish for ring sizes from C_9 to C_{11}. For example, the Ziegler ring closure reaction of α,ω-dinitriles with base fails for rings from C_9 to C_{11} even under high dilution conditions.[17]

Our yields are also remarkable considering the variety of competing pathways open to a thiyl radical intermediate. A thiyl radical must be involved to account for the anti-Markovnikov sense of the addition, since the addition of H_2S to diallyl ether under ionic conditions yields 2,6-dimethyl-1,4-thioxane.[18,19] Clearly the intramolecular radical addition of the S–H bond of dimethylallyl-3-mercaptopropylsilane (**1**) to the carbon–carbon double bond of the allyl group is critical to the success of the reaction. To substantiate this point we prepared **1** independently by the photochemical addition of thiolacetic acid to dimethyldiallysilane followed by hydrolysis of the thiolace-





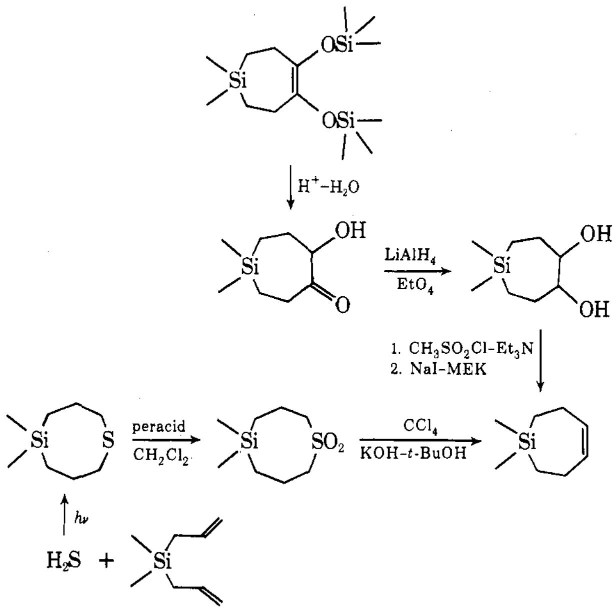
tate with aqueous base. Photolysis of 1 under similar conditions gave comparable yields of 1,1-dimethyl-1-sila-5-thiacyclooctane.

In a related study Surzur has shown that the direction of intramolecular addition of a thiyl radical to a terminal carbon–carbon double bond is strongly influenced by temperature.[20,21] Thus 1-mercapto-5-hexene was cyclized to a mixture of 1-thia-2-methylcyclohexane and 1-thiacycloheptane in which the six-membered ring predominates at high temperature while the seven-membered ring predominates at low temperature (−65°). Surprisingly, in our system in which six-, seven-, and eight-membered rings are all possible the only volatile products detected were the eight-membered rings and uncyclized **1**. Clearly at low temperature formation of the eight-membered ring product must be under irreversible kinetic control.

Successful oxidation of the sulfide to the corresponding sulfone followed by a Ramberg–Backlund reaction afforded 1,1-dimethyl-1-sila-4-cycloheptene in a three-step reaction sequence starting from dimethyldiallylsilane. This is an economical solution to the synthesis of organosilicon heterocycles containing a carbon–carbon double bond.

Thus 1,1-dimethyl-1-sila-5-thiacyclooctane was oxidized to the sulfone by reaction with *m*-chloroperbenzoic acid in dichloromethane at 0° in 95% yield.[22] Treatment of the sulfone with aqueous NaOH in the presence of CCl_4, a modification of the Ramberg–Backlund reaction developed by Meyers,[8,23] led to a 50% yield of 1,1-dimethyl-1-sila-4-cycloheptene. These results are noteworthy, since this reaction usually leads to the corresponding vinylic sulfonic acid when the carbon atoms on either side of the sulfone are primary.[23] Likewise, 1,1-diphenyl-1-sila-5-thiacyclooctane was oxidized to the corresponding sulfone with *m*-chloroperbenzoic acid. The modified Ramberg–Backlund reaction on the sulfone yields 1,1-diphenyl-1-sila-4-cycloheptene in 40% isolated yield.

This reaction permits definitive structure proof that the photoadducts of dimethyldiallylsilane and diphenyldiallylsilane with H_2S are indeed eight-membered rings, since we have prepared both 1,1-dimethyl-1-sila-4-cycloheptene and 1,1-diphenyl-1-sila-4-cycloheptene by independent synthetic routes. Hydrolysis of 1,1-dimethyl-4,5-bis(trimethylsiloxy)-1-sila-4-cycloheptene[1] yields 1,1-dimethyl-5-hydroxy-1-sila-4-cycloheptanone.[24] Reduction of the acyloin with $LiAlH_4$ in ether leads to 1,1-dimethyl-1-sila-4,5-cycloheptanediol in 90% yield. The diol was converted to the dimesylate by reaction with 2 mol of mesyl chloride in the presence of triethylamine.[25] The dimesylate was not purified but was converted directly to the alkene by treatment with NaI in refluxing methyl ethyl ketone in 20% yield.[26,27] The structure of the 1,1-diphenyl-1-sila-5-thiacyclooctane was likewise proved by independent synthesis of the alkene resulting from the Ramberg–Backlund reaction. Dimethyl 4,4-diphenyl-4-sila-1,7-heptanedioate[13] was cyclized using the modified acyloin reaction[2,3] to 1,1-diphenyl-4,5-bis(trimethylsiloxy)-1-sila-4-cycloheptene in 72% yield. The bis silyl enol ether was hydrolyzed to the acyloin in 95% yield. The acyloin was reduced to the diol by treatment with $LiAlH_4$ in THF in high yield. The diol was converted to the dimesylate, which was treated directly with NaI in refluxing methyl ethyl ketone to yield 1,1-diphenyl-1-sila-4-cycloheptene in 37% yield.



Experimental Section

All reactions were carried out under a nitrogen atmosphere. All operations were conducted in an efficient fume hood owing to the toxicity of H_2S and the vile smell of volatile organosulfur compounds. Melting points are uncorrected. Ir spectra were determined as neat liquids or in CCl_4 solution on a Perkin-Elmer 337. They were calibrated against known peaks in a polystyrene film. Nmr spectra were run on a Varian HA-100 using 10% solutions in CS_2. Chloroform, dichloromethane, or tetramethylsilane were used as internal standards. Microanalysis was performed by Elek Microanalytical Laboratory. High-resolution mass spectra were run on an AEI MS-902 instrument. Exact mass determination of the composition of important ions were carried out at resolution of at least 10,000 by peak matching with peaks of known mass of perfluorokerosene: ionizing voltage 70 eV; filament emission 480 μA; source temperature 150°.

1,1-Dimethyl-1-sila-5-thiacyclooctane. A quartz photolysis well was inserted into a 2-l. flask equipped with a Dry Ice–acetone reflux condenser and a fritted gas inlet tube. In this apparatus were placed 50 g (0.36 mol) of dimethyldiallylsilane[28] and 1.5 l. of olefin-free pentane. Purified nitrogen was bubbled through the solution to purge it of air. The solution was cooled to −78° by immersion of the entire apparatus in an isopropyl alcohol–Dry Ice bath. H_2S (10 g, 0.29 mol) was slowly bubbled through the solution while it was being illuminated with a 450-W medium-pressure Hanovia lamp. The addition required 1 hr. Photolysis was continued for an additional 1 hr. The solution was then warmed to room temperature. After removal of pentane, the product was fractionally distilled through a 15-cm Vigreux column. A fraction of bp 115–130° (25 mm) was collected. Final purification was accomplished by glpc on an Apiezon L column (6 ft × 0.25 in.) at 225°. A 25% yield (approximately 6 g) based on recovered starting material was obtained. Ir was characterized by two strong $Si(CH_3)_2$ bands at 1245 and 790 cm^{-1}; nmr s (6 H) δ −0.13, m (4 H) 0.49, m (4 H) 1.61, m (4 H) 2.31. *Anal.* Calcd for $C_8H_{18}SiS$: C, 55.09; H, 10.42. Found: C, 55.09; H, 10.21.

1,1-Dimethyl-1-sila-5-thiacyclooctane 5,5-Dioxide. In a 100-ml three-necked round-bottom flask equipped with a pressure-equalizing addition funnel, a reflux condenser, a magnetic stirring bar, and a thermometer were placed 30 ml of CH_2Cl_2 and 20 g (0.116 mol) of *m*-chloroperbenzoic acid.[22] The solution was cooled to 0° by immersion in a salt–ice bath. 1,1-Dimethyl-1-sila-5-thiacyclooctane (6.5 g, 0.037 mol) dissolved in 5 ml of CH_2Cl_2 was placed in the addition funnel and then added to the well-stirred reaction mixture at a rate such that the temperature did not exceed 5°. After the addition was complete the solution was warmed to room temperature and then heated to reflux for 1 hr. Five grams of Na_2SO_3 was added and stirring was continued for 15 min. The solution was filtered and the CH_2Cl_2 solvent was removed by evaporation under reduced pressure. Final purification was by glpc on an FFAP 2 ft × 0.25 in. column at 215°. Its ir spectrum was characterized by strong SO_2 absorption bands at

1330 and 1140 cm^{-1}; nmr s (6 H) δ 0.02, m (4 H) 0.86, m (4 H) 2.01, m (4 H) 3.04.

1,1-Dimethyl-1-sila-4-cycloheptene. In a dry one-neck 100-ml round-bottom flask equipped with a reflux condenser and a magnetic stirring bar were placed 0.22 g (1.07 mmol) of 1,1-dimethyl-1-sila-5-thiacyclooctane 5,5-dioxide, 3.0 g (0.065 mol) of powdered KOH, 15 ml of dry *tert*-butyl alcohol, and 35 ml of dry CCl_4.[8,23] The mixture was heated for 12 hr at 50° while being stirred. The reaction mixture was transferred to a separatory funnel and 100 ml of ether was added. The organic layer was extracted with three equal volumes of water, dried over anhydrous $MgSO_4$, and filtered, and the solvents were removed by evaporation under reduced pressure. The residue was bulb-to-bulb distilled. Final purification was by glpc on an Apiezon L column (18 ft × 0.25 in.) at 130°. Its ir showed a weak C–C double-bond stretch at 1645 cm^{-1}; nmr (CHF_2Cl solvent) s (6 H) δ 0.06, m (4 H) 0.67, m (4 H) 2.3, m (2 H) 5.8. Its mass spectrum showed a weak parent ion at *m/e* 140, a strong P − 15 ion at *m/e* 125, and a P − 28 ion at *m/e* 112. Calcd for $C_7H_{13}Si$: 125.0786. Found: 125.0756. Calcd for $C_6H_{11}Si$: 112.0708. Found: 112.0697. *Anal.* Calcd for $C_8H_{16}Si$: C, 68.49; H, 11.49. Found: C, 68.54; H, 11.19.

4,4-Dimethyl-4-sila-6-heptene 1-Thiolacetate. In a dry 500-ml round-bottom flask equipped with a reflux condenser and a magnetic stirring bar were placed 167 g (1.15 mol) of dimethyldiallylsilane and 14 g (0.20 mol) of thiolacetic acid. While stirring, the solution was illuminated with a sun lamp for 6 hr. The solution was fractionally distilled through a 15-cm vacuum-jacketed Vigreux column. After removal of unreacted dimethyldiallylsilane, bp 134° (760 mm), the distillation was continued at reduced pressure. A fraction of bp 130–135° (25 mm) was collected. It amounted to 34 g (68%) based on recovered dimethyldiallylsilane. Final purification was accomplished by gplc using an FFAP column (2 ft × 0.25 in.) at 200°. Its ir was characterized by a carbonyl band at 1695 cm^{-1} and a carbon–carbon double-bond stretch at 1640 cm^{-1}; nmr s (6 H) δ −0.17, m (2 H) 0.54, m (4 H) 1.46, s (3 H) 2.19, t (2 H) 2.73, *J* = 7 Hz, m (2 H) 4.71, m (1 H) 5.65. *Anal.* Calcd for $C_{10}H_{20}SiSO$: C, 55.50; H, 9.31. Found: C, 55.33; H, 9.07.

Dimethylallyl-3-mercaptopropylsilane. In a 500-ml round-bottom flask equipped with a reflux condenser and a magnetic stirring bar were placed 23 g (0.106 mol) of 4,4-dimethyl-4-sila-6-heptene 1-thiolacetate, 2 g (0.037 mol) of KOH, and 30 ml of 1:1 ethanol–water. The solution was refluxed for 3 hr after which it was acidified to pH 4.0 using glacial acetic acid. Pentane was added and the solution was extracted twice with water. The organic layer was dried over anhydrous $MgSO_4$ and filtered and the pentane was removed by distillation through a 15-cm Vigreux column: nmr s (6 H) δ −0.15, m (2 H) 0.55, m (5 H) 0.82, m (2 H) 2.38, m (2 H) 4.66, m (1 H) 5.65.

1,1-Diphenyl-1-sila-5-thiacyclooctane. A quartz photolysis well was inserted in a 2-l. flask equipped with a Dry Ice–acetone reflux condenser and a fritted gas inlet tube at the bottom. In this apparatus were placed 50 g (0.19 mol) of diphenyldiallylsilane[29] and 1.5 l. of olefin-free pentane. Purified nitrogen was bubbled through the solution to purge it of air. The solution was cooled to −78° by immersion of the entire apparatus in an isopropyl alcohol–Dry Ice bath. H_2S (10 g, 0.29 mol) was slowly bubbled through the solution while it was being illuminated with a 450-W medium-pressure Hanovia lamp. The addition required 1 hr. Photolysis was continued for an additional 2 hr. The solution was then warmed to room temperature. After removal of pentane by distillation, the product was fractionally distilled through a 15-cm Vigreux column. A fraction of bp 180–220° (0.1 mm) was collected. This fraction was further purified by chromatography on a 10 × 0.5 in. alumina column. The product was eluted with pentane. A 10% yield (approximately 6 g) based on recovered starting material was obtained: nmr m (4 H) δ 1.27, m (4 H) 1.84, m (4 H) 2.50, m (10 H) 7.24. *Anal.* Calcd for $C_{18}H_{22}SiS$: C, 72.42; H, 7.43. Found: C, 72.71; H, 7.54.

1,1-Diphenyl-1-sila-5-thiacyclooctane 5,5-Dioxide. In a 100-ml three-necked round-bottom flask equipped with a pressure-equalizing addition funnel, a reflux condenser, a magnetic stirring bar, and a thermometer were placed 30 ml of CH_2Cl_2 and 5 g (0.0273 mol) of *m*-chloroperbenzoic acid.[22] The solution was cooled to 0° by immersion in a salt–ice bath. 1,1-Diphenyl-1-sila-5-thiacyclooctane (1.45 g, 4.86 mmol) dissolved in 5 ml of CH_2Cl_2 was placed in the addition funnel and was added to the well-stirred reaction mixture at such a rate that the temperature did not exceed 5°. After the addition was complete, the solution was warmed to room temperature and was then heated to reflux for 1 hr. Five grams of Na_2SO_3 was added to destroy excess peracid. Stirring was continued for 15 min. The solution was filtered, and the CH_2Cl_2 solvent was removed by evaporation under reduced pressure. The residue was chromatographed on a 10 × 0.5 in. alumina column, eluting with $CHCl_3$. Ir was characterized by strong SO_2 absorption bands at 1285 and 1100 cm^{-1}; nmr m (4 H) δ 1.50, m (4 H) 2.14, m (4 H) 2.98, m (10 H) 7.32. *Anal.* Calcd for $C_{18}H_{22}SiSO_2$: C, 65.41; H, 6.71. Found: C, 65.70; H, 6.76.

1,1-Diphenyl-1-sila-4-cycloheptene. In a dry 100-ml round-bottom flask equipped with a reflux condenser were placed 0.49 g (1.5 mmol) of 1,1-diphenyl-1-sila-5-thiacyclooctane 5,5-dioxide, 6.0 g (0.11 mol) of powdered KOH, 30 ml of dry *tert*-butyl alcohol, and 50 ml of dry CCl_4.[8,23] The mixture was heated for 12 hr at 50° while being stirred. The reaction mixture was transferred to a separatory funnel, and 30 ml of CH_2Cl_2 was added. The organic layer was washed with three equal volumes of water, dried over anhydrous $MgSO_4$, and filtered, and the solvent was removed by evaporation under reduced pressure. The product was then purified by glpc on an Apiezon L column (18 × 0.25 in.) at 200°, mp 63–63.4°. The ir showed a weak C–C double bond at 1650 cm^{-1}; nmr m (4 H) δ 1.23, m (4 H) 2.35, m (2 H) 5.72, m (10 H) 7.38. The mass spectrum showed a parent ion at *m/e* 264 and an intense P − 28 ion at *m/e* 236. Calcd for $SiC_{18}H_{20}$: 264.1334. Found: 264.1277. Calcd for $SiC_{16}H_{16}$: 236.1021. Found: 236.0997. *Anal.* Calcd for $C_{18}H_{20}Si$: C, 81.76; H, 7.62. Found: C, 81.48; H, 7.54.

1,1-Dimethyl-5-hydroxy-1-sila-4-cycloheptanone.[24] In a 300-ml round-bottom flask equipped with a magnetic stirring bar were placed 19 g (0.06 mol) of 1,1-dimethyl-4,5-bis(trimethylsiloxy)-1-sila-4-cycloheptene,[1] 50 ml of THF, and 40 ml of 2 *N* HCl. The mixture was stirred overnight. The layers were separated. The organic layer was dried over anhydrous $MgSO_4$ and filtered, and the solvent was evaporated. The yield of crude product was 10 g (97%). The compound was purified by distillation through a 10-cm Vigreux column, bp 130° (25 mm) or 50° (0.2 mm). Ir showed a broad OH band at 3450 cm^{-1} and a carbonyl band at 1710 cm^{-1}; nmr s (3 H) δ −0.01, s (3 H) 0.01, m (4 H) 0.7, m (2 H) 1.9, m (2 H) 2.5, t (1 H) 4.2, *J* = 5 Hz.

1,1-Dimethyl-1-sila-4,5-cycloheptanediol. In a dry 500-ml round-bottom three-neck flask, equipped with a pressure-equalizing addition funnel, a magnetic stirring bar, and a reflux condenser was placed 2 g (0.53 mol) of $LiAlH_4$ in 100 ml of anhydrous ether. To this was added 12.2 g (0.07 mol) of crude 1,1-dimethyl-5-hydroxy-1-sila-4-cycloheptanone[24] in 50 ml of anhydrous ether. After 2 hr the reaction was quenched by addition of 10 ml of H_2O. The layers were separated. The ether layer was dried over anhydrous $MgSO_4$ and filtered and the solvents were removed under reduced pressure. This reaction yields 11 g (90%) of crude product. The cis isomer was recrystallized from pentane at −20°; mp 48–49°; nmr s (3 H) δ −0.09, s (3 H) −0.07, m (4 H) 0.55, m (4 H) 1.68, m (2 H) 3.59, s (2 H) 4.0. The singlet at δ 4.0 disappeared after treatment with D_2O.

1,1-Dimethyl-1-sila-4-cycloheptene. In a dry 100-ml flask equipped with a magnetic stirring bar were placed 3.7 g (0.02 mol) of 1,1-dimethyl-1-sila-4,5-cycloheptanediol, 8 ml (0.08 mol) of triethylamine, and 4 ml (0.05 mol) of mesyl chloride in 50 ml of CH_2Cl_2.[25] The mixture was stirred at room temperature overnight. The solution was then poured into 50 ml of water. The layers were separated. The organic layer was dried over anhydrous $MgSO_4$ and filtered and the solvent was removed under reduced pressure. The crude dimesylate (7 g) was dissolved in 100 ml of methyl ethyl ketone, and 11 g (0.8 mol) of NaI was placed in a 250-ml flask equipped with a reflux condenser and a magnetic stirring bar. The reaction was stirred at reflux for 48 hr.[27] The brown solution was cooled, poured into a separatory funnel, and washed with two 50-ml portions of saturated $Na_2S_2O_4$ to remove the I_2 color. The organic layer was then dried over anhydrous $MgSO_4$ and filtered and the solvent was removed by distillation through a 10-cm Vigreux column. A fraction of bp 100–140° was collected (1.6 g). It was further purified by chromatography on a 10 × 0.5 in. alumina column eluted with pentane. In this way 0.63 g (20% yield) was obtained. An analytical sample was purified by glpc on a 15 ft × 0.25 in. Carbowax column at 100°. Its physical and spectral properties were in agreement.

1,1-Diphenyl-4,5-bis(trimethylsiloxy)-1-sila-4-cycloheptene. In a dry 1-l. three-necked round-bottom flask, equipped with a high-speed stirrer, a pressure-equalizing addition funnel, and a reflux condenser were placed 20.0 g (0.9 mol) of Na and 350 ml of dry toluene. The toluene was heated to reflux, at which time stirring was started. To the Na dispersion were added 120 ml (0.9 mol) of trimethylchlorosilane and 64 g (0.2 mol) of dimethyl 4,4-diphenyl-4-sila-1,7-heptanedioate[13] over 2 hr. The reaction mixture was heated at reflux for 2 hr after the addition was complete. The reaction mixture was cooled and filtered under a cone of N_2. The solvent was removed by distillation through a 10-cm Vigreux column at atmospheric pressure. The residue was then distilled. A central fraction of 57 g (72% yield), bp 130° (0.001 mm), was collected. Ir showed a C–C double bond at 1680 cm^{-1}; nmr s (18 H) δ 0.29, m (4 H) 1.4, m (4 H) 2.5, m (10 H) 7.48.

1,1-Diphenyl-5-hydroxy-1-sila-4-cycloheptanone. In a 300-ml round-bottom flask equipped with a magnetic stirring bar were placed 53 g (0.12 mol) of 1,1-diphenyl-4,5-bis(trimethylsiloxy)-1-sila-4-cycloheptene, 75 ml of THF, and 75 ml of 2 *N* HCl. The mixture was stirred overnight. The layers were separated. The organic layer was dried over anhydrous $MgSO_4$ and filtered and the solvent was evaporated. The yield of crystalline product was 35 g (95%), mp 94–97°. Recrystallization from *n*-hexane gave a white solid, mp 96–98°. Ir showed a broad OH band at 3450 cm^{-1} and a carbonyl band at 1710 cm^{-1}; nmr m (4 H) δ 1.45, m (2 H) 2.1, m (2 H) 2.65, broad s (1 H) 3.8, m (1 H) 4.25, m (10 H) 7.19. *Anal.* Calcd for $SiC_{18}H_{20}O_2$: C, 72.93; H, 6.80. Found: C, 72.73; H, 6.60.

1,1-Diphenyl-4,5-dihydroxy-1-silacycloheptane. In a dry 500-ml round-bottom three-necked flask equipped with a pressure-equalizing addition funnel, a magnetic stirring bar, and a reflux condenser was placed 3 g (0.075 mol) of $LiAlH_4$ in 100 ml of ether. In the addition funnel was placed 35.0 g (0.12 mol) of crude 1,1-diphenyl-5-hydroxy-1-sila-4-cycloheptanone in 100 ml of anhydrous THF. This solution was added to the hydride suspension at a rate to maintain reflux. After 2 hr the reaction was quenched by the addition of water. The layers were separated. The organic layer was dried over anhydrous $MgSO_4$ and filtered and the solvent was removed at reduced pressure, resulting in 33 g of a thick yellow oil which solidified on standing: nmr m (8 H) δ 1–2, m (4 H) 3.7, m (10 H) 7.3. Its ir showed two OH bands in CCl_4, one at 3300 cm^{-1} and the other at 3550 cm^{-1}.

1,1-Diphenyl-1-sila-4-cycloheptene. In a dry 50-ml flask equipped with a magnetic stirring bar were placed 1 g (3.4 mmol) of 1,1-diphenyl-1-sila-4,5-cycloheptanediol, 1.4 ml (10 mmol) of triethylamine, and 20 ml of CH_2Cl_2. The solution was cooled to 0° and 0.6 ml (7.5 mmol) of mesyl chloride was added.[25] The mixture was stirred for 2 hr and then poured into 50 ml of H_2O. The layers were separated. The organic layer was dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. The crude dimesylate, 3.0 g (20 mmol) of NaI, and 20 ml of methyl ethyl ketone were placed in a 50-ml flask equipped with a reflux condenser and a magnetic stirring bar.[27] The solution was stirred at reflux for 40 hr; 50 ml of ether was added. The reaction mixture was washed with two 50-ml portions of water and once with a saturated solution of $Na_2S_2O_4$ to disperse the I_2 color. It was dried over anhydrous $MgSO_4$ and filtered and the solvents were removed at reduced pressure. The residue, 610 mg, was then chromatographed through a 10 × 0.5 in. alumina column with *n*-hexane. In this way 330 mg (37% yield) of crystalline olefin was collected. It was recrystallized from 95% ethanol, mp 63°.

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Registry No.—1,1-Dimethyl-1-sila-5-thiacyclooctane, 49592-51-0; dimethyldiallylsilane, 1113-12-8; H_2S, 7783-06-4; 1,1-dimethyl-1-sila-5-thiacyclooctane 5,5-dioxide, 51051-56-0; 1,1-dimethyl-1-sila-4-cycloheptene, 51051-57-1; 4,4-dimethyl-4-sila-6-heptene 1-thiolacetate, 51006-76-9; thiolacetic acid, 507-09-5; dimethylallyl-3-mercaptopropylsilane, 49592-52-1; 1,1-diphenyl-1-sila-5-thiacyclooctane, 51051-58-2; diphenyldiallylsilane, 10519-88-7; 1,1-diphenyl-1-sila-5-thiacyclooctane 5,5-dioxide, 51051-59-3; 1,1-diphenyl-1-sila-4-cycloheptene, 51051-60-6; 1,1-dimethyl-5-hydroxy-1-sila-4-cycloheptanone, 10325-25-4; 1,1-dimethyl-4,5-bis(trimethylsiloxy)-1-sila-4-cycloheptene, 32297-03-3; *cis*-1,1-dimethyl-1-sila-4,5-cycloheptanediol, 51051-61-7; 1,1-diphenyl-4,5-bis(trimethylsiloxy)-1-sila-4-cycloheptene, 51051-62-8; dimethyl 4,4-diphenyl-4-sila-1,7-heptanedioate, 34564-74-4; 1,1-diphenyl-5-hydroxy-1-sila-4-cycloheptanone, 51051-63-9; 1,1-diphenyl-4,5-dihydroxy-1-silacycloheptane, 51051-64-0.

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Preparation of New Nitrogen-Bridged Heterocycles. Reaction of Pyridinium *N*-Imines with α-Haloacrylates in the Presence of Alkali

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Pyridinium *N*-imine hydriodides (**1–5**) reacted with ethyl and methyl α-chlorocinnamates and methyl α-bromocrotonate in the presence of alkali at room temperature to afford the corresponding 1,9a-dihydro-2*H*-pyrido[1,2-*b*]-*as*-triazine derivatives (**11–17**). Structural elucidation of these compounds was accomplished by physical and spectral means and by the conversion of compounds **11** and **16** to the dehydrogenated 2*H*-pyrido[1,2-*b*]-*as*-triazines **20** and **21**.

Pyridinium *N*-imine is a very useful and versatile precursor for preparations of various nitrogen-bridged heterocycles[1] and N-substituted iminopyridinium ylides[2] as described in many reports. In particular, increased attention