frared spectrum of this compound was identical with that of the sample prepared above from androstadienedione (Ia).

4-Methylestra-1,3,5(10)-trien-17-one.—To a solution of 177 mg. of 1-chloro-4-methylestra-1,3,5(10)-trien-17-one (IVa) and 50 mg. of sodium acetate in 50 ml. of 95% ethanol was added 50 mg. of 20% palladium on carbon, and the resulting mixture was hydrogenated at room temperature and atmospheric pressure. One equivalent of hydrogen was absorbed in 15 min. The mixture was filtered and concentrated to dryness under reduced pressure. The residue was extracted with ether, the extracts were concentrated to dryness, and the residue was recrystallized from methanol, giving 129 mg. of colorless crystals, m.p. 191–192°. A mixture of this compound and a sample of 4-methylestra-1,3,5(10)-trien-17-one prepared by an independent synthesis (m.p. 189–191°)[2] melted at 190–192°. The infrared spectra of the two samples were identical when run in both potassium bromide disks and in chloroform solution.

Acknowledgment.—The elementary analyses were performed by Mr. C. E. Childs and the staff of our Microanalytical Laboratory; the spectra and rotations were determined by Dr. J. M. Vandenbelt and the staff of our Physical Chemistry Laboratory. We are indebted to Dr. L. M. Long for his support of this work.

Silicon Heterocyclic Compounds. II. Synthesis of 3-Sila-1-heterocycloheptanes[1]

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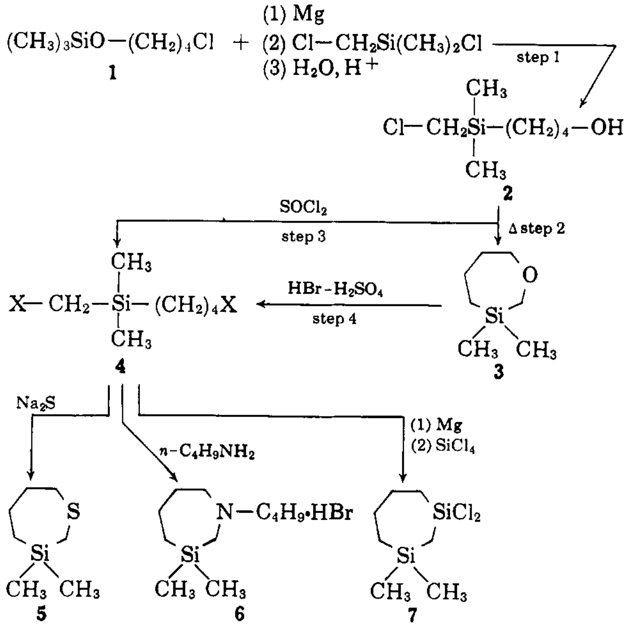
A series of 1-sila-3-heterocycloheptanes of the general formula, $(CH_3)_2\overline{SiCH_2ZCH_2CH_2CH_2CH_2}$, where Z is O (**3**), S (**5**), $NC_4H_9 \cdot HBr$ (**6**), and $SiCl_2$ (**7**), have been prepared. Reaction of $(CH_3)_3SiO(CH_2)_4MgCl$ with $(ClCH_2)SiCl(CH_3)_2$ gave $HO(CH_2)_4Si(CH_3)_2CH_2Cl$ (**2**) after water work-up. Atmospheric distillation of **2** yielded **3**. Reaction of **2** with $SOCl_2$ yielded $X(CH_2)_4Si(CH_3)_2CH_2X$ (**4**, X = Cl), and cleavage of **3** with HBr and H_2SO_4 yielded **4** (X = Br). Preparation of the di-Grignard reagent of **4** (X = Br) and reaction with $SiCl_4$ gave **7**. Reaction of **4** (X = Cl) with Na_2S gave **5** and with *n*-butylamine yielded **6**.

In a previous study[2] we described the synthesis of a new class of stable silicon heterocyclic compounds, the 3-sila-1-heterocyclohexanes. This report is concerned with the extension of the synthetic method to the 3-sila-1-heterocycloheptanes.

The reports of silaheterocycloheptanes are sparse[3]; the parent silacycloheptane and a few of its derivatives have been reported and studied.[4]

The key step in the synthesis of the silaheterocyclohexanes was a silicon hydride addition to a silyl-blocked allyl alcohol. This study differs in that the key intermediate, δ-hydroxybutyl(chloromethyl)dimethylsilane (**2**), was obtained by means of a Grignard reaction (Scheme I). The preparation of 4-(trimethylsiloxy)-1-chlorobutane (**1**), and the chemistry of the corresponding Grignard reagent have been studied by Speier.[5] The reaction of this Grignard reagent with (chloromethyl)dimethylchlorosilane (step 1) was smooth, and the yield of the desired alcohol (**2**) was high (77%). In step 1 the blocking trimethylsilyl group was removed by the acid work-up so that **2** could be isolated directly from the reaction. In contrast to the isolation of γ-hydroxyalkyl(chloromethyl)dimethylsilanes, used for the synthesis of the 3-sila-1-oxacyclohexanes,[2] no difficulty was encountered in the isolation of **2**.

SCHEME I



The ring closure (step 2) leading to 3,3-dimethyl-3-sila-1-oxacycloheptane (**3**) was carried out using a slow atmospheric distillation. As would be expected,[6] the yields in this ring-closure step were low (35–38%). No attempt was made to characterize the residue.

The other 3-sila-1-heterocycloheptanes were obtained using the dihalogen intermediate **4**. δ-Chlorobutyl(chloromethyl)dimethylsilane (**4**, X = Cl) was obtained in a 61% yield by reaction of **2** with thionyl chloride. δ-Bromobutyl(bromomethyl)dimethylsilane (**4**, X = Br) was obtained by the ring cleavage of **3** with hydrobromic acid and sulfuric acid using the proce-

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(1) This work was supported by a grant (GP-315) from the National Science Foundation.

(2) R. J. Fessenden and M. D. Coon, *J. Org. Chem.*, **29**, 1069 (1964).

(3) (a) W. H. Knoth and R. V. Lindsey, *J. Am. Chem. Soc.*, **80**, 4106 (1958); (b) R. H. Krieble and C. A. Burkhard, *ibid.*, **69**, 2689 (1947); (c) W. H. Kohlschutter and G. Jaekel, *Z. Anorg. Allgem. Chem.*, **271**, 185 (1953); (d) H. C. Kaufman, *J. Chem. Eng. Data*, **7**, 556 (1962); *Chem. Abstr.*, **58**, 10229c (1963); (e) K. A. Andrianov, V. I. Pakhomov, and N. E. Lapteva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2039 (1962); *Chem. Abstr.*, **58**, 9112 (1963); (f) M. Wieber and M. Schmidt, *Ber.*, **96**, 1019 (1963).

(4) (a) R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954); (b) **76**, 6015 (1954); (c) J. M. Hersch, U. S. Patent 2,615,033 (1952); *Chem. Abstr.*, **47**, 9344 (1953).

(5) J. L. Speier, *J. Am. Chem. Soc.*, **74**, 1003 (1953).

(6) E. E. Royals, "Advanced Organic Chemistry," Prentice Hall, Inc. New York, N. Y., 1954, p. 171.

dure for the preparation of 1,5-dibromopentane from tetrahydropyran.[7]

Unexpected difficulties were encountered in the attempt to obtain an analytical sample of **4**, X = Br. Preparative gas phase chromatography failed to yield a pure sample owing to cracking of **4**, X = Br, on the column. Repeated distillation failed to remove all impurities; however, both the infrared and the n.m.r. spectra were in agreement with the assigned structure (see Experimental).

Ring closure of **4**, X = Cl, to 3,3-dimethyl-3-sila-1-thiacycloheptane (**5**) was carried out in 11% yield using sodium sulfide by the procedure of Tarbell and Weaver[8] for the preparation of tetramethylene sulfide. The procedure utilizes the insoluble mercuric chloride salt of **5** for preliminary purification. The ring (**5**) was obtained from this salt (not characterized) by steam distillation. Final purification was accomplished by vacuum fractional distillation.

The reaction of **4**, X = Br, and *n*-butylamine leading to 1-butyl-3,3-dimethyl-3-sila-1-azacycloheptane (**6**) was spontaneous and exothermic. The amine hydrobromide, isolated directly from the reaction mixture, was used for analysis. The free tertiary amine was obtained from the mother liquor using a basic work-up procedure followed by distillation.

1,1-Dimethyl-3,3-dichloro-1,3-disilacycloheptane (**7**) was obtained in 50% yield from the di-Grignard reagent of **4**, X = Br, and silicon tetrachloride. The procedure is a modification of that of West[9] who obtained 1,1-dichlorosilacycloheptane in 11% yield from the di-Grignard reagent of 1,5-dibromopentane and silicon tetrachloride.

One attempt was made to extend this synthetic method to the silaheterocyclopentanes. Treatment of 2-(trimethylsiloxy)-1-chloroethane (**8**) with magnesium followed by reaction of the mixture with (chloromethyl)-dimethylchlorosilane yielded only pentamethyl(chloromethyl)disiloxane and not the desired *β*-hydroxyethyl-(chloromethyl)disiloxane (**9**).[10] This observation agrees with the report by Moody[11] that treatment of **8** with magnesium yields ethylene and the magnesium salt of trimethylsilanol.

Experimental[12]

δ-Hydroxybutyl(chloromethyl)dimethylsilane.—To a Grignard reagent prepared from 250 g. (1.4 moles) of 4-trimethylsiloxy-1-chlorobutane[6] was added 200 g. (1.4 moles) of (chloromethyl)dimethylchlorosilane. The mixture was heated at reflux for 2 days, then decomposed by the addition of 6 *N* hydrochloric acid. The organic layer was separated, and the water layer was extracted with three 100-ml. portions of ether. The organic material was combined, washed with saturated sodium bicarbonate solution until effervescence ceased, then with 100 ml. of water, and finally dried with magnesium sulfate. Fractional distillation yielded 193 g. (77%) of the δ-hydroxybutylsilane, b.p. 95° (2.8 mm.), n^{27}D 1.4640; infrared bands at 3.00, 7.15, 8.5, 9.75, 3.45, 9.45, and 11.80 μ.

Anal. Calcd. for $C_7H_{17}ClOSi$: C, 46.20; H, 9.42; Cl, 19.68; Si, 15.50. Found: C, 46.35; H, 9.22; Cl, 19.91; Si, 15.33.

3,3-Dimethyl-3-sila-1-oxacycloheptane.—In a 250-ml. round-bottomed flask was placed 52.1 g. (0.29 mole) of δ-hydroxybutyl-(chloromethyl)dimethylsilane. The material was distilled at atmospheric pressure while the distillate was collected upon solid sodium bicarbonate. The distillation was conducted at a rate such that the boiling point of the distillate did not exceed 180°. The distillation required *ca.* 5 hr., and 26 g. of residue remained. No attempt was made to characterize the residue. The distillate was allowed to stand over the sodium bicarbonate overnight, then was decanted, and the solid bicarbonate was washed with ether. Fractional distillation yielded 14.5 g. (35%) of the silaoxacycloheptane, b.p. 57–58° (17 mm.), n^{24}D 1.4531. The analytical sample was obtained using a preparative gas phase chromatography column.

Anal. Calcd. for $C_7H_{16}OSi$: C, 58.33; H, 11.11; Si, 19.44. Found: C, 58.15; H, 11.14; Si, 19.22.

The infrared spectrum of the product was in agreement with the assigned structure and exhibited the characteristic Si–CH_3 band at 8.0 and the C–O band at 9.1 μ. Other bands were observed in the spectrum at 3.45, 3.55, 6.85, 7.10, 8.15, 8.50; 8.70, 9.25, 9.75, 10.25, 10.70, 11.45, and 12.00 μ.

δ-Chlorobutyl(chloromethyl)dimethylsilane.—To 155 g. (1.3 moles) of thionyl chloride in a 500-ml. round-bottomed flask was added, over a period of 1 hr., 234 g. (1.3 moles) of δ-hydroxybutyl-(chloromethyl)dimethylsilane. After the addition was complete, the reaction mixture was heated at reflux for an additional hour, then distilled without work-up to yield 178 g. of material boiling at 220–225°. The distillate was diluted with ether, washed with three 50-ml. portions of saturated sodium bicarbonate solution and 50 ml. of water, and then dried with magnesium sulfate. Fractional distillation yielded 158 g. (71.5%) of the δ-chlorobutylsilane, b.p. 227–229°, $n^{24.5}$D 1.4650.

Anal. Calcd. for $C_7H_{16}Cl_2Si$: C, 42.21; H, 8.04; Cl, 35.68. Found: C, 42.13; H, 8.07; Cl, 35.74.

δ-Bromobutyl(bromomethyl)dimethylsilane.—In a 1-l. round-bottomed flask were placed 67.4 g. (0.47 mole) of 3,3-dimethyl-3-sila-1-oxacycloheptane, 138 g. of concentrated sulfuric acid, and 473 g. of 48% hydrobromic acid. The reaction mixture was heated at reflux for 12 hr., then worked up according to the procedure outlined by Andrus.[7] Upon distillation there was obtained 119 g. (88%) of the δ-bromobutylsilane, b.p. 129–130° (2.5 mm.), n^{21}D 1.5031. Redistillation [b.p. 97–98° (0.9 mm.)] failed to yield an analytical sample. A center cut of the redistilled material was subjected to preparative gas chromatographic separation at a column temperature of 200°; however, the material underwent pyrolytic cracking. The same observations were obtained from a second preparation. The infrared spectrum of the center cut showed bands at 3.45, 7.00, 7.20, 8.00 (7.9 sh), 8.20, 8.80, 10.50, and 11.80 μ. The bands at 3.45, 8.00, and 11.80 μ were strong. The n.m.r. spectrum[13] of this sample (15% solution in CCl_4) showed bands at δ 3.25 (triplet, $J = 7$ c.p.s.), 2.35 (singlet), 1.2 to 2.0 (broad multiplet), 0.5 to 0.8 (unresolved multiplet), and 0.20 (singlet). The integrated areas under these bands were in the following ratios: 1.9:2.0:4.2:1.9:6.0. The band assignments are the following: δ 3.25 ($-CH_2-\mathit{CH}_2-Br$), 2.35 ($Si-\mathit{CH}_2-Br$), 1.2 to 2.0 ($Si-CH_2-\mathit{CH}_2-\mathit{CH}_2-CH_2Br$); 0.5 to 0.8 ($Si-\mathit{CH}_2-CH_2-$), and 0.2 [$-Si(CH_3)_2-$].

1,1-Dichloro-3,3-dimethyl-1,3-disilacyloheptane.—A Grignard reagent prepared from 48.5 g. (0.18 mole) of δ-bromobutyl(bromomethyl)dimethylsilane and 8.1 g. (0.34 g.-atom) of magnesium turnings was added slowly over a 2-hr. period to 29.7 g. (0.17 mole) of silicon tetrachloride dissolved in 500 ml. of ether. After the addition had been completed, the reaction mixture was heated at reflux for 2 days. The magnesium salts were removed by suction filtration using Filter Cel. The filtrate was then con-

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(7) D. W. Andrus, *Org. Syn.*, **23**, 67 (1943).

(8) D. S. Tarbell and C. Weaver, *J. Am. Chem. Soc.*, **63**, 2939 (1941).

(9) R. West, *ibid.*, **76**, 6012 (1954).

(10) Even if **9** had been obtained from this reaction it is doubtful that the over-all synthesis would have been successful, owing to the facile cleavage of the *β*-hydroxyalkylsilanes in the presence of acidic reagents [F. C. Whitmore, L. H. Sommer, J. R. Gold, and R. E. Van Strien, *ibid.*, **69**, 1551 (1947)].

(11) L. S. Moody, *ibid.*, **72**, 5754 (1950).

(12) All boiling points and melting points are uncorrected. Distillations were carried out using a 2-ft. modified Podbielniak column (*cf.* J. Cason and H. Rapaport, "Laboratory Text in Organic Chemistry," 2nd Ed., Prentice Hall, Inc., Englewood Cliffs, N. J., 1962, p. 289). Infrared spectra were run using a Beckman IR-5 spectrophotometer using thin films. Microanalyses were carried out by the Berkeley Microanalytical Laboratory, Berkeley, Calif. Silicon analyses were carried out in this laboratory using the wet-ash method [see C. Eaborn, "Organosilicon Compounds," Academic Press, Inc., New York, N. Y., 1960, p. 500, for general references]. Preparative gas chromatographic separations were accomplished using a 15-ft. silicone column built specifically for the Aerograph A-60c unit by the Wilkens Instrument and Research Co.

(13) The n.m.r. spectrum was run using a Varian A-60 spectrophotometer. Bands are reported in parts per million downfield from tetramethylsilane employed as an external reference.

centrated and the residue was distilled under vacuum to yield 19.0 g. (50%) of the disilacycloheptane, b.p. 79–80° (3.2 mm.), n^{24}_{D} 1.4822. An analytical sample (n^{24}_{D} 1.4850) was obtained using the preparative gas chromatographic column.

Anal. Calcd. for $C_7H_{16}Cl_2Si_2$: C, 37.00; H, 7.05. Found: C, 36.93; H, 6.94.

1-Butyl-3,3-dimethyl-3-sila-1-azacycloheptane.—A mixture of 31.7 g. (0.11 mole) of δ-bromobutyl(bromomethyl)dimethylsilane and 17.1 g. (0.22 mole) of *n*-butylamine was placed in a 100-ml. round-bottomed flask. A thermometer was placed through the condenser into the reaction mixture. Reaction was initiated by warming the mixture to 40°, at which temperature a slow but spontaneous exothermic reaction raised the temperature of the mixture to 183°. After completion of the spontaneous reaction, the mixture was heated to a temperature of 215° for 5 min., then allowed to cool to room temperature. The semisolid material was transferred to a beaker and an equal volume of ethanol (95%) was added. After chilling in an ice bath, crystals formed. Filtration and recrystallization from ethanol (95%) yielded 4.5 g. of the amine hydrobromide, m.p. 166.5–168°.

Anal. Calcd. for $C_{11}N_{26}BrNSi$: C, 47.14; H, 9.28; N, 5.00; Si, 10.00. Found: C, 47.02; H, 9.22; N, 4.91; Si, 10.05.

The filtrate was made basic with 8 *N* sodium hydroxide, and organic material was extracted with two 25-ml. portions of ether. After drying with magnesium sulfate, fractional distillation yielded 7.2 g. of the free amine, b.p. 72–75° (3.8 mm.), $n^{23.5}_{\mathrm{D}}$ 1.4600. The infrared spectrum of the free amine was in agreement with the assigned structure and showed bands at 3.45 and 3.60 (C–H), 7.85, 8.0 ($Si–CH_3$), 8.45 (C–N), 11.45, 11.90, and 12.55 μ. No band was observed in the N–H region of the spectrum. The over-all yield of the amine and amine hydrobromide was 43%.

3,3-Dimethyl-3-sila-1-thiacycloheptane.—In a 500-ml. round-bottomed flask were placed 27.2 g. (0.11 mole) of sodium sulfide (dissolved in 50 ml. of water), 200 ml. of ethanol (95%), and 21.7 g. (0.11 mole) of δ-chlorobutyl(chloromethyl)dimethylsilane. The mixture was heated at reflux for 20 hr., then distilled to dryness. A saturated solution of mercuric chloride (about 600 ml.) was added to the distillate until no further precipitation was noted. The precipitate was filtered using suction and transferred to a 2-l. flask, and 1 l. of water was added. The mixture was steam distilled and *ca.* 600 ml. of distillate was collected. The distillate was extracted with three 100-ml. portions of petroleum ether (b.p. 30–60°). Fractional distillation yielded 2.0 g. (11.6%) of the silathiacycloheptane, b.p. 82–83° (13.0 mm.), $n^{24.5}_{\mathrm{D}}$ 1.5054. In one run an attempted atmospheric distillation resulted in decomposition. The infrared spectrum showed bands at 3.45, 7.2, 8.0, 9.3, and 12.0 μ.

Anal. Calcd. for $C_7H_{16}SSi$: C, 52.50; H, 10.00; S, 20.00. Found C, 52.20; H, 9.90; S, 19.85.

Attempted Preparation of β-Hydroxyethyl(chloromethyl)dimethylsilane.—In a 1-l. three-necked round-bottomed flask were placed 27.3 g. (1.1 g.-atoms) of magnesium turnings and 75 ml. of ether. To this mixture was added over a period of 2 hr. 175 g. (1.1 moles) of 2-trimethylsiloxy-1-chloroethane.[14] After the addition had been completed, the reaction mixture was heated at reflux overnight. Then was added 156 g. (1.1 moles) of (chloromethyl)dimethylchlorosilane over a period of 5 min., and the mixture was heated at reflux for 24 hr. The mixture was then filtered and the filtrate was treated with water, then extracted with three 100-ml. portions of ether. Fractional distillation of the organic material yielded 95.3 g. (48.5%) of pentamethyl-(chloromethyl)disiloxane, b.p. 150–153°, n^{22}_{D} 1.4114 (lit.[15] b.p. 151.7–151.8°, n^{20}_{D} 1.4106).

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(15) R. H. Krieble and J. R. Elliott, *ibid.*, **67**, 1810 (1945).

The Synthesis of Bicyclic Ketols from Cyclohexanones

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Reaction conditions are defined for the preparation of ketols by Robinson annelation of cyclohexanones. The *cis*-ketol II and the *trans*-ketol III are formed stereoselectively from 2-methylcyclohexanone and cyclohexanone using an equimolar quantity of methyl vinyl ketone. The ketol II is a convenient source of 10-methyl-1(9)-octalone-2 (I). The scope and stereochemistry of the Michael–aldol reaction sequence is discussed.

In the course of synthetic work we required various homologs of octalone I. Although the Robinson annelation reaction[1,2] provides a direct route to fused ring ketones, the application of this method to cyclohexanones such as 2-methylcyclohexanone[3] has proved generally unsatisfactory.[4] For example, the Robinson synthesis of 10-methyl-1(9)-octalone-2 (I),[3a] and variations thereof,[3b–g] proceeds in low yield, requires a two- or threefold excess of 2-methylcyclohexanone,[3] and affords a product of questionable purity.[3h,5] We undertook a study of this reaction in an effort to discover a reasonable correlation between yield and reaction conditions. Numerous attempts to improve the yield of octalone I by varying the solvent, temperature, ratio of reactants, and nature and quantity of the basic catalyst proved unsuccessful. We then investigated the possibility of effecting the condensation between 2-methylcyclohexanone and methyl vinyl ketone under conditions which might allow the isolation of a ketol intermediate.[2] We eventually found that slow addition of methyl vinyl ketone to an equimolar quantity of 2-methylcyclohexanone at −10° in the presence of a catalytic amount of ethanolic sodium ethoxide gave crystalline ketol II, in 50–55% yield. Under the same conditions cyclohexanone was converted to the ketol III (17% yield), dihydrocarvone gave an epimeric mixture of ketols IV and V (49% yield), and 2,6-dimethylcyclohexanone afforded an impure product (11%) containing ketol VI which was characterized by conversion to octalone VII.

Crude ketol III was accompanied by impurities which, on the basis of infrared and p.m.r. spectra, appeared to consist of diketone VIII and bridged ketol IX. These contaminants could be separated from ketol III,

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(5) The following refractive index values have been recorded for octalone I: n^{16}_{D} 1.5341,[3a] n^{19}_{D} 1.5154,[3b] n^{28}_{D} 1.5060,[3c] n^{25}_{D} 1.5203,[3d] n^{19}_{D} 1.5190.[3g]