exo-**1-Azabicyclo[2.2.1]heptan-3-ol** (**4**).—Compound **3** (1.0 g, 7.6 mmol) was cyclodehydrated over 5.0 g of Woelm basic alumina at 310° and a nitrogen flow rate of 17 ml min^{-1} as described for the synthesis of 3-quinuclidinol,[14] except that a vertical column was used. The product was collected in 25 ml of 50% benzene–ethanol, which was evaporated to give a tan solid. Two recrystallizations from cyclohexane–ethanol followed by a sublimation (50° at 0.1 μ for 5 hr) gave 0.26 g (33%) of **4** as a white solid, mp 128–129°.

Anal. Calcd for $C_6H_{11}NO$: C, 63.7; H, 9.8; N, 12.4; mol wt, 113.12. Found: C, 63.5; H, 9.8; N, 12.1; mol wt, 113.12 (mass spectrum).

A picrate was obtained as yellow prisms, mp 176–177° (acetone–ether).

Anal. Calcd for $C_{12}H_{14}N_4O_8$: C, 42.1; H, 4.1. Found: C, 41.8; H, 4.4.

1-Azabicyclo[2.2.1]heptan-3-one (**5**).—The *exo* alcohol **4** (3.0 g, 27 mmol) was oxidized with chromic acid (6.0 g, 60 mmol) as described for the synthesis of tropan-6-one;[15] except that the reaction mixture was kept at about 67° for 40 hr, and the acetic acid (125 ml) was then removed under reduced pressure. The product was obtained as a yellow oil which crystallized in the condenser during distillation (bp 71°, 4 mm) to give 1.2 g of **5**, a white solid: mp 26–28°; ir (CCl_4) 1760 cm^{-1} (C=O); neut equiv 114 (theory 111). The cold trap was rinsed with chloroform and added to the pot residue, which upon attempted sublimation gave an additional 0.6 g (total yield 62%) of **5** as a liquid, otherwise identical (ir, glpc) with the solid product.

A picrate, mp 202–205° (acetone–ether), was identical (ir) with a picrate, mp 203–204° (ethanol) previously obtained (unpublished)[11] in poor yield from the Dieckmann condensation (and subsequent decarboxylation) of 1-carbethoxymethyl-3-carbethoxypyrrolidine.

Anal. Calcd for $C_{12}H_{12}N_4O_8$: C, 42.4; H, 3.6; N, 16.5. Found[11]: C, 42.6; H, 3.8; N, 16.4.

endo-**1-Azabicyclo[2.2.1]heptan-3-ol** (**6**).—The ketone **5** (1.6 g, 14 mmol) in 24 ml of ethanol was shaken with 0.16 g of platinum dioxide at 50 psig of hydrogen for 5.5 hr at room temperature in a Parr hydrogenator, then filtered and evaporated to give 1.6 g (99%) of product (**6**) as a hygroscopic solid, mp 81–90°, which appeared to be both epimerically and chemically pure by glpc and ir examination. However, the melting point of this initial product was raised considerably by recrystallization, which suggests that traces of retained solvent or water may have been present. Thus, when the product was dissolved in 1.2 l. of cyclohexane and 15 ml of ethanol, and allowed to evaporate at room temperature down to 300 ml, there was obtained 0.57 g of white needles, mp 135–139°. Two recrystallizations from cyclohexane gave **6**, mp 140–142°, mol wt 113.12 (mass spectrum, theory 113.12), picrate mp 202–203° (ether).

Anal. Calcd for $C_{12}H_{14}N_4O_8$: C, 42.1; H, 4.1. Found: C, 42.0; H, 3.9.

1-Azabicyclo[2.2.1]heptane (**7**).—The ketone **5** was hydrogenolyzed as described,[16] then filtered, concentrated, treated with concentrated sodium hydroxide, and extracted with ether. Glpc analysis showed the ether solution to consist of **7**, with a trace of the alcohol **6**. The ir spectrum of **7**, collected from the gas chromatograph, was identical with that of the authentic product, prepared as described.[3b,12] When the ether solution was directly distilled into an ethereal picric acid solution, the volatile **7** codistilled and precipitated as the picrate, mp 277.5° (lit.[3] mp 274°, 285°). Compound **7** was also obtained in 50% yield, isolated as the picrate, by cyclodehydration of 4-hydroxymethylpiperidine,[4] as described for **4**, above.

Comparative Physical Data.—For compounds **4**, **5**, **6**, and **7**, glpc retention times (minutes) for an artificial mixture at 215°, on an 8 ft × 0.25 in. column of 13% Carbowax 20M on 60–80 mesh Gas-Chrom P, 90 ml min^{-1} (He), were as follows: **7**, 0.9; **5**, 2.9; **4**, 5.8; **6**, 6.1. The pK_a values at 0.0050 ionic strength were 10.7, 7.16, 9.38, and 9.76, respectively. For *exo* and *endo*-norborneol, glpc retention times on the above column at 155° and 100 ml min^{-1} were 7.9 and 8.4 min, respectively. Ir data follow (0.001 *M* CCl_4, 2 cm cell), OH band: **4**, 3625 cm^{-1}, half-band width 16 cm^{-1}; **6**, 3628 and 21 cm^{-1}; *exo*-norborneol, 3622 and 17 cm^{-1}; *endo*-norborneol, 3626 and 26 cm^{-1}. The norborneol values differ slightly from those previously recorded.[10] Nmr data follow (20% $CDCl_3$, internal TMS), CH–OH: **4**, τ 6.38, half-band width 10 cps; **6**, 5.75 and 20; *exo*-norborneol, 6.27 and 11; *endo*-norborneol, 5.78 and 17.

(14) H. S. Aaron, O. O. Owens, P. D. Rosenstock, S. Leonard, S. Elkin, and J. I. Miller, *J. Org. Chem.*, **30**, 1331 (1965).
(15) J. B. Jones and A. R. Pinder, *J. Chem. Soc.*, 615 (1959).
(16) L. P. Reiff and H. S. Aaron, *Tetrahedron Lett.*, 2329 (1967).

Registry No.—**1a**, 21472-88-8; **2**, 21473-14-3; **3**, 21492-03-5; **3** (picrate), 21473-15-4; **4** (*exo*), 21473-16-5; **4** (*exo*) (picrate), 21473-17-6; **5**, 21472-89-9; **5** (picrate), 21472-90-2; **6** (*endo*), 21473-18-7; **6** (*endo*) (picrate), 21473-19-8.

Acknowledgment.—We thank the following members of these Laboratories for providing the indicated data: C. A. Andreason (titration), L. W. Daasch (mass spectra), C. P. Ferguson (dilute-solution ir), H. Klapper (nmr), I. Master (uv), and R. L. Young, Jr. (norborneol samples).

Synthesis of 1,1-Diethoxy-2-(trimethylsilyl)-1-sila-2-azacyclopentane

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Organosilicon compounds containing two or more Si–N bonds have a great tendency toward cyclization. In accordance, a variety of such heterocyclic compounds and their methods of preparation are well known.[1-4] However, compounds with $>Si(CH_2)_{3-6}N$-ring structures are limited and are reported only in a few places[5,6] in the literature. In this Note, we have made such a heterocyclic compound named 1,1-diethoxy-2-(trimethylsilyl)-1-sila-2-azacyclo-pentane (A) by the following methods.

"A" was first obtained when we distilled a reaction mixture resulting from reaction 1 on a 36-in. spinning-band column under a N_2 atmosphere. Under slow distillation, B and C decomposed and formed A as one of their products. A had a boiling point (210°) and a

$$(C_2H_5O)_3SiCH_2CH_2CH_2NH_2 + Me_3SiCl + (C_2H_5)_3N \longrightarrow (C_2H_5O)_3SiCH_2CH_2CH_2NHSiMe_3 + (C_2H_5O)_3SiCH_2CH_2CH_2N(SiMe_3)_2 + (C_2H_5)_3NHCl \quad (1)$$

B C

glpc retention time close to those of 3-aminopropyltriethoxysilane (bp 214° as we determined); thus, if a reaction mixture contains both, it is a difficult task to separate them. However, *ca.* 95% pure A can be obtained by repeated spinning-band distillation and a spectro-quality sample by using preparative gas chromatography.

(1) B. J. Aylett, *Organometal. Chem. Rev.*, **3**, 151 (1968).
(2) W. Fink, *Angew. Chem. Intern. Ed. Engl.*, **5** (5), 760 (1966).
(3) U. Wannagat, *Pure Appl. Chem.*, **13** (1–2), 263 (1966).
(4) K. A. Andrianov and L. M. Khananashvili, *Organometal. Chem. Rev.*, **2**, 141 (1967).
(5) J. L. Speier, U. S. Patent 3,146,250 (1964), and U. S. Patent 3,170,941 (1965).
(6) J. W. Ryan, presented at the Symposium on Silicon–Nitrogen Chemistry, University of Wisconsin, Madison, Wis., April 1968.

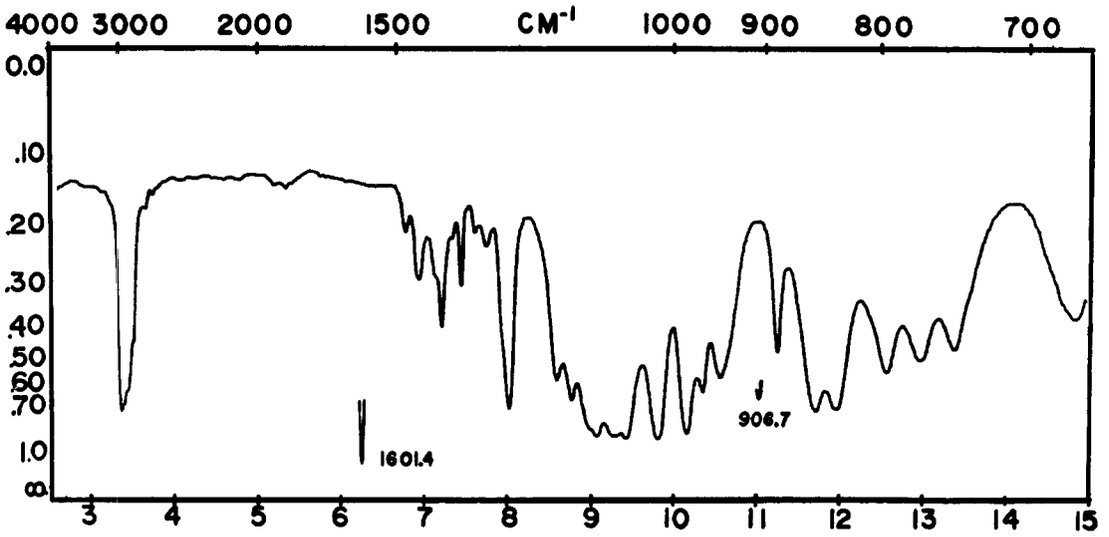


Figure 1.—Infrared spectrum of 1,1-diethoxy-2-(trimethylsilyl)-1-sila-2-azacyclopentane, thin film.

We have found that B and C also decomposed into A when they were heated with ammonium sulfate. C yields A and trimethylethoxysilane as the only products, as shown by eq 2. B gave A, 3-aminopropyltriethoxysilane and trimethylethoxysilane as the products. Evidently B had rearranged into C and the starting aminosilane first, as shown in eq 3. C was formed, then decomposed in accordance with eq 2.

$$(C_2H_5O)_3SiCH_2CH_2CH_2N(SiMe_3)_2 \longrightarrow (C_2H_5O)_2\underbrace{SiCH_2CH_2CH_2N}_{A}SiMe_3 + (C_2H_5O)SiMe_3 \quad (2)$$

$$(C_2H_5O)_3SiCH_2CH_2CH_2NHSiMe_3 \longrightarrow (C_2H_5O)SiCH_2CH_2CH_2N(SiMe_3)_2 + (C_2H_5O)_3SiCH_2CH_2CH_2NH_2 \quad (3)$$

Although reaction 2 gave A in good yield and high purity, it requires B as the starting material, which is tedious to make either by reaction 1 or Kumada's[7] method (eq 4). We, therefore, did not pursue these reactions any further; instead we tried the transamination reaction commonly used for preparation of silazanes

$$(C_2H_5O)_3SiH + CH_2{=}CHCH_2N(SiMe_3)_2 \longrightarrow (C_2H_5O)_3SiCH_2CH_2CH_2N(SiMe_3)_2 \quad (4)$$

with the hope that C would be formed first by transamination reaction, then decomposed to A in accordance with eq 2. It proved to be the best method. When a mixture of 3-aminopropyltriethoxysilane, hexamethyldisilazane, and ammonium sulfate was heated under a flow of N_2, the reaction took place readily in accordance with eq 5. The course of the reaction was followed by periodic titration of the evolved ammonia with standard hydrochloric acid. At the end of the reaction, low-boiling substances were removed by evacuating the system at room temperature for a few hours. A distilled over at 54° (0.5 mm), yield 66%.

$$(C_2H_5O)_3SiCH_2CH_2CH_2NH_2 + Me_3SiNHSiMe_3 \xrightarrow[\text{heat}]{(NH_4)_2SO_4} (C_2H_5O)_2\underbrace{SiCH_2CH_2CH_2N}_{A}SiMe_3 + NH_3\uparrow + C_2H_5OSiMe_3 \quad (5)$$

An attempt to synthesize 1,1-diethoxy-1-sila-2-azacyclopentane, $(C_2H_5O)_2\underbrace{SiCH_2CH_2CH_2NH}$, by heating 3-aminopropyltriethoxysilane and ammonium sulfate was not successful. All that we obtained were ethyl alcohol and an unidentified polymer. This result seems to coincide with what has been reported for the compound $\underbrace{SiNHCH_2CH_2NH}$[8,9] which is also unstable and forms only a polymer.

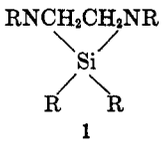
The infrared spectrum of A is different from that of B and C. B and C, analogous to many reported silazanes,[9,10] exhibit a strong absorption at 910 cm^{-1} for the stretching frequency of the Si–N bond. The ir spectrum of A, shown in Figure 1, does not have an absorption at 910 cm^{-1}; instead it has two strong absorptions at 985 and 1020 cm^{-1}. For organosilyl-substituted cyclosilazanes, Fink[11] has assigned a strong absorption in the 1005–1040-cm^{-1} region as characteristic of structures containing N-silylated silicon–nitrogen ring compounds. This characteristic absorption was also observed by Breed, Elliott, and Budde[12,13] in a series of organosilyl-substituted cyclodisilazanes. The absorption at 1020 cm^{-1} exhibited by A probably arises from a structure of this nature. Five-membered cyclosilazanes were also reported[10,11] to have an absorption at 1350 cm^{-1} derived from ring vibrations. We have observed this absorption, although rather small, in the ir spectrum of A. This absorption is not observed in the ir spectra of either B or C.

The nmr spectrum of A shows good agreement with the proposed cyclic structure. The measurements are summarized in Table I. The chemical shifts of the

(7) K. Shina and M. Kumada, *Mem. Iac. Eng. Osaka City Univ.*, **1**, (1959); *Chem. Abstr.*, **55**, 15341 (1961).

(8) R. Minne and E. G. Rochow, *J. Amer. Chem. Soc.*, **82**, 5625 (1960).
(9) F. A. Henglein and K. Lienhand, *Makromol. Chem.*, **32**, 218 (1959).
(10) C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **5**, 2055 (1966).
(11) W. Fink, *Helv. Chem. Acta*, **45**, 1081 (1962).
(12) L. W. Breed and R. L. Elliott, *Inorg. Chem.*, **2** (5), 1069 (1963).
(13) L. W. Breed, W. L. Budde, and R. L. Elliott, *J. Organometal. Chem.*, **6**, 676 (1966).

methylene proton in a series of ring compounds with the general structure of 1 were reported[14] to be about 0.3



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ppm downfield from the methylene proton in the linear silylethylenediamine compounds. We have obtained a similar result by a comparison of the chemical shifts of the protons in A with those in C. The chemical shifts of all of the protons of C were found at 0.00 [$(CH_3)_3Si$–], 2.60 (–NCH_2), 1.40 (NCH_2CH_2), 0.30 (–CH_2Si–), 3.69 (–OCH_2), and 1.08 (–OCH_2CH_3). With the $(CH_3)_3Si$– group in each compound as the standard, the ring protons in A were apparently further downfield than their equivalent protons in C. The ethoxy protons in both compounds were found to have practically identical chemical shifts.

TABLE I

NMR DATA OF $(CH_3CH_2O)_2SiCH_2CH_2CH_2NSi(CH_3)_3$

Chemical shifts, δ	Multiplicity	Rel intensity	Assignment
0.00	Singlet	9	$(CH_3)_3Si$–
3.64	Quartet	4	–CH_2–O–
1.08	Triplet	6	CH_3CH_2O–
2.81	Triplet	2	–CH_2N–
1.67	Quintet	2	–CH_2CH_2N–
0.41	Triplet	2	–$SiCH_2$–

Unlike its oxygen analogs,[15-18] which polymerize on standing, A is a stable compound, able to react with butyllithium without cleavage of the ring unit to form 1,-1-dibutyl-2-trimethylsilyl-1-sila-2-azacyclopentane and 1-butyl-1-ethoxy-2-trimethylsilyl-1-sila-2-azacyclopentane in 77% yield.

Experimental Section

Reagent grade 3-aminopropyltriethoxysilane was purchased from Union Carbide Corp.; practical grade chlorotrimethylsilane and 1,1,1,3,3,3-hexamethyldisilazane were purchased from Eastman Chemical Co.; and *n*-butyllithium from Foote Mineral Co., Exton, Pa. All were used without further purification. Reagent grade triethylamine was dried over KOH before use.

Boiling points are uncorrected. Fractional distillations were run on a Nester/Faust spinning-band column (Nester/Faust Manufacturing Corp., Newark, Del.) with a 36 in. × 10 mm column using a gold-plated monel spinning band.

Analytical glpc was run on a F & M Model 500 chromatograph using a 0.25 in. × 6 ft stainless steel column packed with 10% SE-30 on 60–80 Chromosorb W. Preparative glpc was run on a F & M Model 770 using a 0.75 in. × 8 ft stainless steel column packed with 10% SE-52 on 60–80 Chromosorb W.

Elemental analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, N. Y.

I. 1,1-Diethoxy-2-(trimethylsilyl)-1-Sila-2-Azacyclopentane. A. Reaction of 3-Aminopropyltriethoxysilane, Chlorotrimethylsilane, and Triethylamine.—Chlorotrimethylsilane (91 g, 0.84 mol) was added, with stirring and a flow of N_2 gas, to a solution of 3-aminopropyltriethoxysilane (94 g, 0.42 mol), triethylamine (150 ml), and xylene (300 ml). The N_2 was led through a Dry Ice cooling trap before discharge. After addition, the mixture was heated on a steam bath for 24 hr. The triethylamine hydrochloride formed was removed by filtration and washed with heptane. The filtrate and heptane washings were combined and distilled on a Vigreux column to remove low-boiling, fuming substances, then on a spinning-band column. A fraction [88 g, bp 160–190° (1 atm)] was identified by glpc as a mixture of low-boiling substances, 1,1-diethoxy-2-(trimethylsilyl)-1-sila-2-azacyclopentane, and 3-aminopropyltriethoxysilane. Repeated spinning-band distillation gave relatively pure 1,1-diethoxy-2-(trimethylsilyl)-1-sila-2-azacyclopentane (22 g, 21%), bp 210°, purified for analysis by preparative glpc.

Anal. Calcd for $C_{10}H_{25}O_2NSi_2$: C, 48.58; H, 10.12; N, 5.67; Si, 22.67; mol wt, 247. Found: C, 48.58, 48.84; H, 10.38, 10.07; N, 5.70, 5.73; Si, 22.84, 22.90; mol wt, 250, 256.

Vacuum distillation of the residue gave a fraction (8 g) distilling at 108–110° (0.5 mm) [270° (1 atm)] identified as N,N-bis-(triethylsilyl)-3-aminopropyltriethoxysilane, 5.2% [lit.[19] bp 143°] (8 mm).

Anal. Calcd for $C_{15}H_{39}O_3NSi_3$: C, 49.32; H, 10.68; N, 3.84; Si, 23.01, mol wt, 365. Found: C, 49.61, 49.48; H, 10.63, 10.64; N, 3.82, 4.02; Si, 23.12, 23.20; mol wt, 365 (mass spectrometry).

B. Decomposition of N,N-Bis(trimethylsilyl)-3-aminopropyltriethoxysilane with Ammonium Sulfate.—N,N-bis(trimethylsilyl)-3-aminopropyltriethoxysilane (36 g, 0.1 mol) under N_2 was heated to near boiling and ammonium sulfate (*ca.* 1 g) was then added. Upon addition, a low-boiling substance distils off immediately. The solution was cooled and upon vacuum distillation gave 16 g (65.3%) of 1,1-diethoxy-2-(trimethylsilyl)-1-sila-2-azacyclopentane [bp 54–57° (0.5 mm)] identified by ir, nmr, boiling point, and glpc retention time. Glpc analysis indicated that it contained *ca.* 5% 3-aminopropyltriethoxysilane.

C. Reaction of 3-Aminopropyltriethoxysilane, Hexamethyldisilazane, and Ammonium Sulfate.—A mixture of 3-aminopropyltriethoxysilane (94 g, 0.42 mol), hexamethyldisilazane (100 g, 0.62 mol), and ammonium sulfate (5 g) in a flask equipped with a magnetic bar, a 1-ft Vigreux column, Claisen adaptor, Friedrichs condenser, and N_2 inlet and outlet tubes was heated to initiate the reaction. The NH_3 gas generated was led through an ice–water cooling trap into 200 ml of water. Standard HCl solution (3.22 *N*) was used to periodically neutralize the ammonia to the phenolphthalein end point. In 7 hr 0.43 mol of ammonia (100%) was collected. After the reaction mixture was cooled to room temperature, the ice–water cooling trap and the titration apparatus were replaced with a Dry Ice cooling trap. A weighed flask was placed on the take-off arm of the Claisen adaptor and the reaction mixture was vacuum distilled. The low boiling point substances were removed at room temperature (3–4 hr). The expected compound (70 g, 66%, purity near 98%) distilled over at 53° (0.5 mm). Its identity was confirmed from its ir, nmr, boiling point, and glpc retention time.

D. Decomposition of N-(Trimethylsilyl)-3-aminopropyltriethoxysilane with Ammonium Sulfate.—N-(Trimethylsilyl)-3-aminopropyltriethoxysilane (100 g, 0.34 mol) and ammonium sulfate (5 g) were refluxed for 1 hr. Vacuum distillation gave a liquid (57.4 g), bp 60–77° (0.2 mm). Glpc indicated that it consisted of A (37%) and 3-aminopropyltriethoxysilane (63%).

II. Synthesis of N-(Trimethylsilyl)-3-aminopropyltriethoxysilane and N,N-Bis(trimethylsilyl)-3-aminopropyltriethoxysilane.—To a mixture of 3-aminopropyltriethoxysilane (190 g, 0.85 mol), triethylamine (145 g, 1.4 mol), and xylene (200 ml) in the same apparatus as that used in IA was added chlorotrimethylsilane (171 g, 1.58 mol). The reaction mixture was heated on a steam bath for 2 hr and stirred at room temperature overnight.

The triethylamine hydrochloride was removed by filtration under N_2 and washed with heptane. The filtrate and washing solution were combined and distilled on a Vigreux column to remove low boiling point substances. The residue in the distilling flask stood overnight and was filtered again to remove a second crop of triethylamine hydrochloride and the filtrate was vacuum distilled on a spinning-band column, giving 194 g of N-(trimethylsilyl)-3-aminopropyltriethoxysilane (87%), bp 88–90° (0.5 mm), 247° (1 atm). One more distillation gave a pure sample.

(14) D. Kummer and J. D. Baldeschweiler, *J. Phys. Chem.*, **67**, 98 (1963).
(15) J. L. Speier, M. P. David, and B. A. Eynon, *J. Org. Chem.*, **25**, 1637 (1960).
(16) V. G. Rossmy and G. Koerner, *Makromol. Chem.*, **73**, 85 (1964).
(17) W. H. Knoth, Jr., and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **80**, 4106 (1958).
(18) K. A. Andrianov, V. I. Pakhomov, and N. E. Lapteva, *Dokl. Akad. Nauk SSSR*, **151**, No. 4, 849 (1963).
(19) V. Bazant, V. Chvalovsky, and J. Rathousky, "Organosilicon Compounds," Part 2(2), Academic Press, London and New York, 1965, p 408.

Anal. Calcd for $C_{12}H_{31}O_3NSi_2$: C, 49.15; H 10.58; Si, 19.11; N, 4.78; mol wt, 293. Found: C, 49.59, 48.66; H, 10.69, 10.60; Si, 18.09, 17.80; N, 5.30, 5.03; mol wt, 293 (mass spectrometry).

The residue, vacuum distilled, gave 27 g of N,N-bis(trimethylsilyl)-3-aminopropyltriethoxysilane, bp 108–110° (0.5 mm). Its identity was confirmed by ir and glpc retention time which was identical with that of the sample obtained from expt IA.

III. Alkylation of 1,1-Diethoxy-2-(trimethylsilyl)-1-sila-2-azacyclopentane.—A butyllithium solution (139 cc, 0.23 mol) was added slowly in a stream of N_2 to a solution of 1,1-diethoxy-2-(trimethylsilyl)-1-sila-2-azacyclopentane (28 g, 0.113 mol) and 100 ml of anhydrous ether. After addition, the solution was stirred at room temperature for 2 hr. The white solid was filtered off and washed with hexane. The filtrate and wash solution were combined and distilled, giving 22.8 g of colorless liquid [bp 75–80° (0.1 mm)]. Glpc analysis indicated two components separated by gas chromatography. Compound I (21.8%) was assigned as 1-ethoxy-1-butyl-2-(trimethylsilyl)-1-sila-2-azacyclopentane.

Anal. Calcd for $C_{12}H_{29}NOSi_2$: C, 55.59; H, 11.20; Si, 21.62; N, 5.41; mol wt, 259. Found: C, 56.08, 55.84; H, 11.52, 11.40; Si, 20.78, 20.58; N, 5.60, 5.41; mol wt, 259 (mass spectrometry).

Compound II (54.9%) was assigned as 1,1-dibutyl-2-(trimethylsilyl)-1-sila-2-azacyclopentane.

Anal. Calcd for $C_{14}H_{33}NSi_2$: C, 61.99; H, 12.18; Si, 20.66; N, 5.17; mol wt, 271. Found: C, 61.73, 61.73; H, 12.33, 12.09; Si, 20.54, 20.47; N, 5.44, 5.31; mol wt, 271 (mass spectrometry).

IV. Attempts to Synthesize 1,1-Diethoxy-1-sila-2-azacyclopentane.—3-Aminopropyltriethoxysilane (94 g, 0.32 mol) and ammonium sulfate (9 g) were heated to reflux under N_2 for 2 hr. Upon vacuum distillation, 40 g of 3-aminopropyltriethoxysilane was recovered. Further distillation decomposed the reaction mixture to ethyl alcohol and an unidentified polymer. The ethyl alcohol was identified by its ir spectrum.

Registry No.—A, 21297-72-3; N-(trimethylsilyl)-3-aminopropyltriethoxysilane, 21297-73-4; 1-ethoxy-1-butyl-2-(trimethylsilyl)-1-sila-2-azacyclopentane, 21-297-74-5; 1,1-dibutyl-2-(trimethylsilyl)-1-sila-2-azacyclopentane, 21297-75-6; N,N-bis(trimethylsilyl)-3-aminopropyltriethoxysilane, 17940-89-5.

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Preparation of Cycloheptanone *via* a Lewis Acid Catalyzed Cyclization of 6-Heptenoyl Chloride to β-Chlorocycloheptanone

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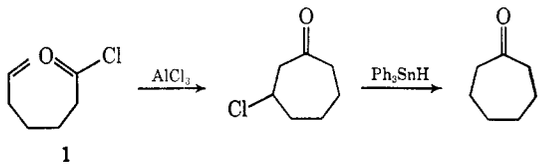
We have found that cycloheptanone can be prepared in fair yield by triphenyltin hydride reduction[2] of β-chlorocycloheptanone, which was obtained from the aluminum trichloride catalyzed cyclization of 6-heptenoyl chloride. For three runs which used 0.3 g of



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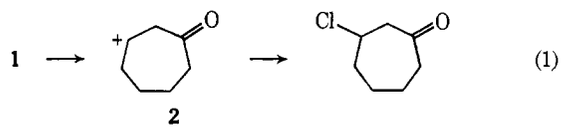
6-heptenoyl chloride, the yield of cycloheptanone was 53 ± 4% based on glpc analysis using cyclohexanone as an internal standard. The identity of the cycloheptanone was proved by nmr, ir, and glpc analyses of the colorless oil which was obtained by vacuum distillation of the crude product from a run which used 3 g of 6-heptenoyl chloride. Glpc analysis showed that the distilled product contained >80% cycloheptanone and <2% 2-methylcyclohexanone.

Kuivila[2] has clearly shown that the triphenyltin hydride reduction of an alkyl chloride usually goes without any carbon skeleton rearrangements. Therefore the cycloalkanones obtained from the triphenyltin hydride reduction should possess the same carbon structures as the chlorocycloalkanones from the cyclization reaction. Further confirmation that the crude product from the aluminum trichloride catalyzed cyclization of 6-heptenoyl chloride was mainly β-chlorocycloheptanone was obtained by nmr and ir analyses. Cyclization of the olefin to form a carbonium ion followed by attack of a chloride ion on this cation



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should lead to β-chlorocycloheptanone. Comparison of the nmr spectrum of an authentic sample of α-chlorocycloheptanone with that of the crude product provided convincing evidence for the absence of the α isomer.

The formation of the cyclooctanone by triphenyltin hydride reduction of the products of the aluminum trichloride catalyzed cyclization of 7-octenoyl chloride was attempted. Under conditions similar to those used for the cyclization of 6-heptenoyl chloride and even under conditions 50 times more dilute, the 7-octenoyl chloride formed mainly tars. Attempts using carbon disulfide–stannic chloric, benzene–stannic chloride, carbon disulfide–aluminum trichloride, and ether–stannic chloride with high dilution met with similar results. Glpc analysis of the triphenyltin reduction of the products from the aluminum trichloride treatment of 7-octenoyl chloride showed that less than 0.1% cyclooctanone or methylcycloheptanones was produced.

Discussion

Most olefin cyclization reactions, either under solvolytic conditions,[3,4] acid-catalyzed conditions,[3,5] or other conditions that generate cations,[6] lead to five- and six-membered rings. Recently several groups of workers have reported the formation of seven-membered rings

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(2) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 77 (1964).

(3) W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968), and references cited therein.

(4) W. S. Trahanovsky, M. P. Doyle, and P. D. Bartlett, *J. Org. Chem.*, **32**, 150 (1967), and references cited therein.

(5) (a) M. F. Ansell and M. H. Palmer, *Quart. Rev.* (London), **18**, 211 (1964); (b) J. C. Bardhan and K. C. Bhattachargya, *Chem. Ind.* (London), 800 (1951); (c) O. Riobe, *Compt. Rend.*, **248**, 2774 (1959); (d) J. J. Beereboom, *J. Org. Chem.*, **30**, 4230 (1965); (e) W. F. Erman and H. C. Kretschmar, *ibid.*, **33**, 1545 (1968).

(6) (a) G. Büchi, E. Koller, and C. W. Perry, *J. Amer. Chem. Soc.*, **86**, 5646 (1964); (b) E. E. Van Tamelen and E. J. Hessler, *Chem. Commun.*, 411 (1966); (c) R. Breslow, J. T. Groves, and S. S. Olin, *Tetrahedron Lett.*, 4717 (1966); (d) L. Cassar, G. P. Chiusoli, and M. Foa, *ibid.*, 285 (1967); (e) T. Inukai and T. Kojima, *J. Org. Chem.*, **32**, 869, 872 (1967).