was extracted with petroleum ether (bp 30-60°) and the crude product was removed by filtration. Recrystallization was accomplished from ethyl acetate-petroleum ether (bp 30-60°): yield 2.2 g; mp 187-188.5°; ir the same as that described for the compound above; molecular weight by mass spectrometry, 198 (calcd 198); nmr (DMSO-d_6) δ 7.37 (s, 5, phenyl), 12.12 (s, 1, -OH) and 12.54 ppm (s, 1, -OH). The product gave a red complex with nickelous acetate, indicating an *anti*-glyoxime structure.[8]

Anal. Calcd for $C_8H_7ClN_2O_2$: C, 48.38; H, 3.55; N, 14.11. Found: C, 48.12; H, 3.43; N, 13.82.

α-Hydroxyiminophenylacethydroximoyl Chloride (6) from α-Ketophenylacethydroximoyl Chloride (9).[11]—The procedure appearing in the literature[11] for reacting α-ketophenylacethydroximoyl chloride (9) and hydroxylamine hydrochloride without base yielded α-hydroxyiminophenylacethydroximoyl chloride melting at 187-189° dec and having an ir spectrum superimposable upon that of the sample obtained by hydrogen chloride addition to the nitrile oxide **2a**.

Dehydrohalogenation of α-Hydroxyiminophenylacethydroximoyl Chloride (6).[5a]—When a suspension of α-hydroxyiminophenylacethydroximoyl chloride in chloroform was shaken with neutral or pH 4.0 buffered solutions, or sodium bicarbonate solutions, dehydrohalogenation was effected smoothly.[5a] The chloroform solutions were then dried azeotropically by first passage through phase-separating paper (Whatman 1 PS) followed by concentration under vacuum. The prominent band in the ir spectrum of these solutions is the nitrile oxide. Removal of the remaining solvent caused spontaneous dimerization of the nitrile oxide to a furazan oxide[5a] as shown by the disappearance of the nitrile oxide band (2288 cm^{-1}) in the ir and the appearance of strong double bond absorption associated with the furazan oxide ring (1600 cm^{-1}).[7,12] The dimer structure was also confirmed by mass spectrometry which showed a molecular ion at *m/e* 324. When the nitrile oxide was generated by simply shaking the hydroximoyl chloride **6** in chloroform-water,[13] the chloroform solution, after drying and concentration as above, showed a strong nitrile oxide absorption in its ir spectrum, but again dimerization occurred when all of the solvent was removed.

Attempted Methylations of 4-Phenylfurazan 2-Oxide.—Samples of 4-phenylfurazan 2-oxide were recovered unchanged after dissolution and refluxing in methyl iodide for 1 hr, or after dissolution in dimethyl sulfate with heating at 100° for 1 hr. Evaporation of the reactants under high vacuum and comparison of the ir spectra and melting points after recrystallization of the residues established that no reaction had occurred.

Irradiation of 4-Phenylfurazan 2-Oxide.—A 1% ethereal solution of 4-phenylfurazan 2-oxide in a quartz flask was subjected to 7 hr irradiation at 253 nm from 16 75-watt low pressure mercury vapor lamps at 35-40°. Ir analyses showed no decomposition of the starting material when the experiment was performed either under a nitrogen atmosphere or with air bubbling through the solution.

1:1 Adduct between 4-Phenylfurazan 2-Oxide (or α-Hydroxyimino-*anti*-phenylacetonitrile Oxide) and Mesityl Oxide.—A solution of 1 g of 4-phenylfurazan 2-oxide in 10 ml of mesityl oxide was allowed to stand for 20 days. Evaporation of the solvent left 1.7 g of a solid residue which was recrystallized from chloroform-petroleum ether (bp 30-60°). The melting point was erratic between 150 and 166°, perhaps indicating a mixture of the two possible isomers although the compound was homogeneous on tlc; ir ($CHCl_3$) 3571, 1709, 1370, and 1353 cm^{-1}; mass spectral molecular weight 260 (calcd 260).

Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.41; H, 6.13; N, 10.39.

Registry No.—**1**, 7707-64-4; **2a**, 32971-22-5; **3**, 32971-23-6; **6**, 33021-14-6; **7**, 1456-22-0; 1:1 adduct of **1** and mesityl oxide, 33015-59-7.

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[12] J. H. Boyer, D. I. McCane, W. J. McCarville, and A. T. Tweedie, *J. Amer. Chem. Soc.*, **75**, 5298 (1953); N. E. Boyer, G. M. Czerniak, H. S. Gutowski, and H. R. Snyder, *ibid.*, **77**, 4238 (1955).

[13] In solution there is the following equilibrium: $RC(=NOH)C(=NOH)Cl \rightleftarrows RC(=NOH)C\equiv N^+-O^- + HCl$.[11] Since the hydroximoyl chloride is insoluble in chloroform in contrast to the nitrile oxide which is soluble, simply shaking the hydroximoyl chloride with chloroform-water yields a chloroform solution of the nitrile oxide.

Synthesis of 1-Aza-2-silacyclopentane Compounds

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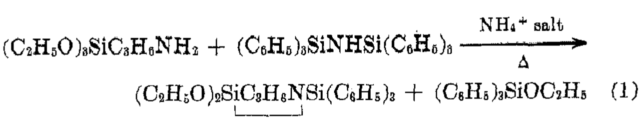
Ethoxy derivatives of the 1-aza-2-silacyclopentane[1a] ring system were prepared and their reactions investigated. Cyclotri(2-ethoxy-1-aza-2-silacyclopentane) reacted with ethanol to form 3-aminopropyltriethoxysilane and with ethyllithium and phenyllithium to form cyclotri[2-ethyl- (or phenyl-) 1-aza-2-silacyclopentane].

In our previous note,[1b] we have reported the synthesis of 1-(trimethylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane. The ring structure in this compound showed remarkable stability toward cleavage either on standing (which resulted in cleavage of its oxygen analogs)[2-5] or in Grignard reactions in which the two side ethoxy groups were replaced. Since the 1-aza-2-silacyclopentane ring system has received little attention, we extended our study to the synthesis of additional derivatives of this rather stable silazane structure.

Hexaphenyldisilazane and 3-aminopropyltriethoxysilane were allowed to react as indicated in eq 1. Fifty



$$(C_2H_5O)_3SiC_3H_6NH_2 + (C_6H_5)_3SiNHSi(C_6H_5)_3 \xrightarrow[\Delta]{NH_4^+\ salt} (C_2H_5O)_2SiC_3H_6NSi(C_6H_5)_3 + (C_6H_5)_3SiOC_2H_5 \quad (1)$$

A

per cent of the theoretical amount of ammonia was evolved after heating the reaction mixture for 4 days and a small amount of 1-(triphenylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane (A) was obtained upon work-up. The silazane was found to have been primarily converted into ethoxytriphenylsilane. Since steric effect[6-8] from bulky substituents on nitrogen atoms has been claimed as a main factor in preventing amine

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[1] (a) In order to conform to the IUPAC nomenclature system, the name of the ring system, -1-sila-2-azacyclopentane used in our previous report,[1b] was changed to 1-aza-2-silacyclopentane. (b) T. T. Tsai and C. J. Marshall, Jr., *J. Org. Chem.*, **34**, 3676 (1969).

[2] J. L. Speier, M. P. David, and B. A. Eynon, *J. Org. Chem.*, **25**, 1637 (1960).

[3] V. C. Rossney and G. Koerner, *Makromol. Chem.*, **73**, 85 (1964).

[4] W. H. Knoth, Jr., and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **80**, 4106 (1958).

[5] K. A. Andrianov, V. I. Pakhonlov, and H. E. Lapteva, *Dokl. Akad. Nauk SSSR*, **151**, 849 (1963).

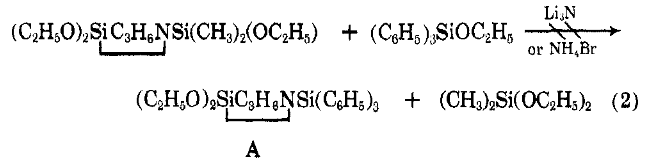
[6] L. W. Breed and R. L. Elliott, *Inorg. Chem.*, **3**, 1624 (1964).

[7] C. H. Yoder and J. J. Zuckerman, *ibid.*, **4**, 116 (1965).

[8] S. H. Langer, S. Connel, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

exchange reactions between silazane and amines, it seems quite likely that the three bulky phenyl groups on a silicon atom exerted a similar effect in this reaction. In addition to the isolation of compound A, ethoxytriphenylsilane, and ammonia, there was evidence from mass spectrometric analysis of the formation of two other products with molecular weights of 387 [possibly corresponding to cyclotri(2-ethoxy-1-aza-2-silacyclopentane), trimer D] and 516 [possibly corresponding to cyclotetra(2-ethoxy-1-aza-2-silacyclopentane), tetramer E], respectively.

An attempt to synthesize compound A by the reaction of 1-ethoxydimethylsilyl-2,2-diethoxy-1-aza-2-silacyclopentane with ethoxytriphenylsilane, as illustrated in eq 2, was unsuccessful.

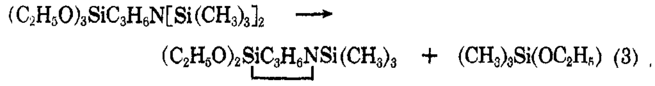


$$(C_2H_5O)_2SiC_3H_6NSi(CH_3)_2(OC_2H_5) + (C_6H_5)_3SiOC_2H_5 \xrightarrow[\text{or } NH_4Br]{Li_3N} (C_2H_5O)_2SiC_3H_6NSi(C_6H_5)_3 + (CH_3)_2Si(OC_2H_5)_2 \quad (2)$$

A

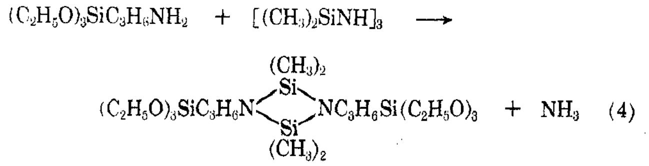
The reaction of hexamethylcyclotrisilazane and 3-aminopropyltriethoxysilane in the presence of a catalytic amount of ammonium bromide yielded 1-(ethoxydimethylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane (B) (eq 4 and 5) as the main product. In this reaction, it was noted that (a) ammonia evolution was rapid and stoichiometric; (b) the yield of B was 49% and only a small amount of diethoxydimethylsilane was formed; and (c) the formation of high molecular weight substances containing ethoxydimethylsilyl end groups (see Table I) occurred.

Based on the above observations and a reported reaction (1) as shown by eq 3, we suggest the following mechanism.



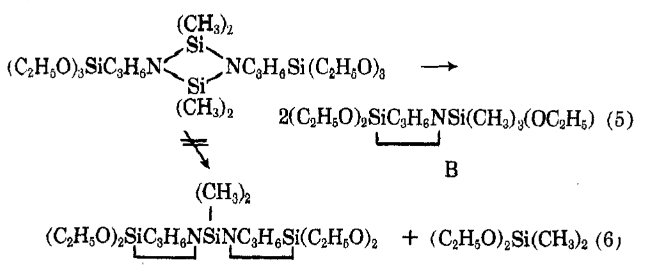
$$(C_2H_5O)_3SiC_3H_6N[Si(CH_3)_3]_2 \longrightarrow (C_2H_5O)_2SiC_3H_6NSi(CH_3)_3 + (CH_3)_3Si(OC_2H_5) \quad (3)$$

(1) Transamination



$$(C_2H_5O)_3SiC_3H_6NH_2 + [(CH_3)_2SiNH]_3 \longrightarrow (C_2H_5O)_3SiC_3H_6N{<}[Si(CH_3)_2]_2{>}NC_3H_6Si(C_2H_5O)_3 + NH_3 \quad (4)$$

(2) Condensation



$$(C_2H_5O)_3SiC_3H_6N{<}[Si(CH_3)_2]_2{>}NC_3H_6Si(C_2H_5O)_3 \longrightarrow 2(C_2H_5O)_2SiC_3H_6NSi(CH_3)_2(OC_2H_5) \quad (5)$$

B

$$\not\longrightarrow (C_2H_5O)_2SiC_3H_6N\overset{(CH_3)_2}{Si}NC_3H_6Si(C_2H_5O)_2 + (C_2H_5O)_2Si(CH_3)_2 \quad (6)$$

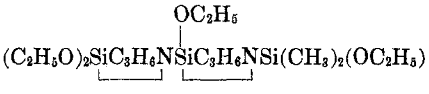
C

It was surprising to find that C, which would be expected to form (eq 6), was not isolated. A liquid, isolated by preparative glpc, had a molecular weight and elementary analysis corresponding to that calculated for C. However, its nmr spectrum indicated the presence of three different ethoxy groups suggesting a possible structure M as indicated below.

Table I

m/e	Possible structures
350	$(C_2H_5O)_2SiC_3H_6NMe_2SiNHMe_2SiOC_2H_5$ or $(C_2H_5O)_2SiC_3H_6N(C_2H_5O)_2SiC_3H_6NH_2$
351[a]	$(C_2H_5O)_2SiC_3H_6NMe_2SiOMe_2SiOC_2H_5$
387[a]	$\left[-\overset{OC_2H_5}{Si}C_3H_6N-\right]_3$ (trimer D)
406[a]	$(C_2H_5O)_2SiC_3H_6N\overset{OC_2H_5}{Si}C_3H_6NMe_2SiOC_2H_5$
516	$\left[-\overset{OC_2H_5}{Si}C_3H_6N-\right]_4$ (tetramer E)
535	$(C_2H_5O)_2SiC_3H_6N\overset{OC_2H_5}{Si}C_3H_6N\overset{OC_2H_5}{Si}C_3H_6N\overset{Me_2}{Si}OC_2H_5$

[a] Isolated and had molecular weight and elementary analysis.

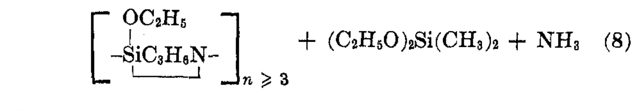


$$(C_2H_5O)_2SiC_3H_6N\overset{OC_2H_5}{Si}C_3H_6NSi(CH_3)_2(OC_2H_5)$$

M

In a separate experiment, the residue obtained after removal of B was analyzed by mass spectrometric techniques. Among numerous *m/e* peaks observed in the spectrum there were six peaks (Table I) to which structures could be assigned.

In spite of the fact that 3-aminopropyltriethoxysilane reacted with hexamethylcyclotrisilazane in one case and with hexaphenyldisilazane in the other, both reactions produced trimer D and tetramer E, along with other products. The formation of these oligomers appeared to have resulted from some secondary condensations reactions. For example, B may have decomposed in the presence of a trace of lithium nitride, in accordance with eq 7, to yield such oligomers.



$$(C_2H_5O)_2SiC_3H_6NSi(CH_3)_2(OC_2H_5) \longrightarrow \left[-\overset{OC_2H_5}{Si}C_3H_6N-\right]_{n \geqslant 3} + (C_2H_5O)_2Si(CH_3)_2 \quad (7)$$

B

Trimer D was prepared in 26% yield by refluxing 3-aminopropyltriethoxysilane and hexamethylcyclotrisilazane under nitrogen with a trace of lithium nitride until no more ammonia generated over (eq 8).

$$(C_2H_5O)_3SiC_3H_6NH_2 + [(CH_3)_2SiNH]_3 \longrightarrow \left[-\overset{OC_2H_5}{Si}C_3H_6N-\right]_{n \geqslant 3} + (C_2H_5O)_2Si(CH_3)_2 + NH_3 \quad (8)$$

Because of the slow evolution of ammonia and the low yield of A as well as high yield of ethoxytriphenylsilane obtained, it is believed that trimer D and tetramer E formed from the reaction of hexaphenyldisilazane and 3-aminopropyltriethoxysilane were not formed by condensation of A, but by a series of displacement and condensation reactions as shown in eq 9 and 10.

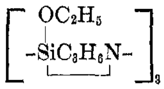
$$(C_2H_5O)_3SiC_3H_6NH_2 + 2(C_6H_5)_3SiNHSi(C_6H_5)_3 \longrightarrow [(C_6H_5)_3SiNH)_2(C_2H_5O)SiC_3H_6NH_2 + 2(C_6H_5)_3SiOC_2H_5 \quad (9)$$

$$[(C_6H_5)_3SiNH]_2(C_2H_5O)SiC_3H_6NH_2 \longrightarrow$$

$$\left[-\overset{\mathrm{OC_2H_5}}{\overset{|}{\mathrm{Si}}}\mathrm{C_3H_6N}-\right]_{n \geqslant 3} + (C_6H_5)_3SiNHSi(C_6H_5)_3 + NH_3 \quad (10)$$

An attempt to separate trimer D from the reaction mixture containing ethoxytriphenylsilane was unsuccessful. In view of the fact that Wannagat, *et al.*,[9] had converted silicon–oxygen compounds into silazanes by treating alkoxysilanes with alkali metal derivatives of amines, we used lithium nitride instead of the hexaphenyldisilazane in the reaction with 3-aminopropyltriethoxysilane and obtained trimer D in 30% yield. An attempt to isolate the tetramer E was unsuccessful.

Although evidence from elemental analysis and molecular weight determinations [obtained from mass spectrometry (387) and from vapor osmometry (384.28, 380.32)] are in agreement with the proposed structure



$$\left[-\overset{\mathrm{OC_2H_5}}{\overset{|}{\mathrm{Si}}}\mathrm{C_3H_6N}-\right]_3$$

D

for trimer D, the nmr spectrum of the compound is not as well defined as those of monocyclic compounds. The peaks arising from the ethoxy groups consist of two sets of triplets centered at δ 1.03 and 1.06, and two sets of quartets centered at δ 3.53 and 3.58, respectively. The anomalous observation is believed to result from the presence of asymmetric silicon atoms.

Further evidence for the proposed structure of the trimer D has been obtained from the following chemical reactions: (1) alcoholysis of trimer D; (2) alkylation and arylation of trimer D.

(1) Trimer D was found to react slightly with anhydrous ethanol. However, it gave a 79% yield of 3-aminopropyltriethoxysilane when allowed to react with ethanol in the presence of a catalytic amount of lithium ethoxide.

(2) Trimer D reacted readily with ethyllithium or phenyllithium (prepared from bromoethane or bromobenzene and lithium) to apparently form cyclotri(2-ethyl-1-aza-2-silacyclopentane) in 45% yield and cyclotri(2-phenyl-1-aza-2-silacyclopentane) in 64% yield.

Because of the unusual cyclic structures, the nmr spectra of the presumed cyclotri(2-ethyl-1-aza-2-silacyclopentane) and cyclotri(2-phenyl-1-aza-2-silacyclopentane) were found to be very complex. Attempts to analyze the spectra in detail were thus unsuccessful. Evidence for the proposed structures was based on elemental analyses, molecular weight determinations, and alcoholysis, the reaction of cyclotri(2-ethyl-1-aza-2-silacyclopentane) with ethanol in which 3-aminopropyldiethoxyethylsilane was the only isolable product. We believe that the corresponding product, 3-aminopropyldiethoxyphenylsilane, was also formed in the reaction of cyclotri(2-phenyl-1-aza-2-silacyclopentane) with ethanol. Evidence for its identity was obtained from a comparison of its ir and nmr spectra with that of its ethyl analog. A quantitative identification was not made owing to the following reasons. (1) The compound was not so stable as its ethyl analog. It could not be obtained pure even after several purifications by glpc. (2) When the sample was introduced into the mass spectrometer through a heated inlet system (240°), the highest peak in the mass spectrum occurred at *m/e* 207. A small molecular ion peak at *m/e* 253, in addition to the peak at *m/e* 207, was observed only when a special injection was made directly into the ion source chamber. It is unknown at the present time if the *m/e* peak corresponding to 207 is due to F (mol wt 207). If this is the case, the com-

$$C_2H_5O(C_6H_5)\underbrace{SiCH_2CH_2CH_2NH}$$

F

pound must be formed from decomposition in the mass spectrometer, because its presence is not indicated by its ir and nmr spectra.

Experimental Section

Reagent grade 3-aminopropyltriethoxysilane was purchased from Union Carbide Corp., New York, N. Y., hexamethylcyclotrisilazane from Peninsular ChemResearch Inc., Gainesville, Fla., and lithium nitride from Foote Mineral Co., Exton, Pa. All reagents were used without further purification. Hexaphenyldisilazane (mp 174–175°) was prepared by refluxing chlorotriphenylsilane and lithium nitride in THF solution for 48 hr and recrystallizing the product from absolute ethanol.

Analytical glpc's were 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.

Elemental, mass (obtained on a CEC 21-110B mass spectrometer), and nmr spectral analyses (Varian A-56/60A spectrometer, operating at 60 Mc) were performed by the Analytical Branch, Air Force Materials Laboratory. Boiling points of all compounds reported are uncorrected.

1-(Triphenylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane.—A mixture of 3-aminopropyltriethoxysilane (9.4 g, 0.043 mol), hexaphenyldisilazane (17.0 g, 0.032 mol), and ammonium chloride (trace) was heated under nitrogen for 4 days. The gas generated from the reaction was periodically neutralized by standard HCl solution (2.17 *N*) to the methyl red end point and a total of 0.016 mol of ammonia was collected. After the reaction mixture was allowed to cool to room temperature, hexane (30 ml) was added. The insoluble hexaphenyldisilazane (3.0 g) was removed by filtration and identified by its ir spectrum and melting point. The filtrate was concentrated and vacuum distilled. The first fraction (15.6 g), bp 110–165° (0.06 mm), was identified by its ir spectrum as ethoxytriphenylsilane. One crystallization from hexane gave a white solid, mp 58–63° (lit.[10] mp 65°). The second fraction, bp 168–222° (0.06 mm), was a yellow liquid which was taken up in hexane and which afforded 0.61 g of 1-(triphenylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane upon cooling. Upon recrystallization from hexane the solid product gave white crystals, mp 99–101°.

Anal. Calcd for $C_{25}H_{31}NO_2Si_2$: C, 69.28; H, 7.16, N, 3.20; Si, 12.92; mol wt, 433. Found: C, 68.82, 69.16; H, 7.21, 7.02; N, 3.31, 3.15; Si, 12.82, 12.67; mol wt, 449, 452 (osmometry), 433 (mass spectrometry).

The residue from vacuum distillation was analyzed by mass spectrometry and found to contain compounds with *m/e* peaks of 304 [$(C_6H_5)_3SiOC_2H_5$], 433 (A), 387 (trimer D), and 516 (tetramer E) as well as other peaks for which assignment could not be made.

Attempted Synthesis of 1-(Triphenylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane.—A mixture of 1-(ethoxydimethylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane (11.1 g, 0.04 mol), ethoxytriphenylsilane (12.2 g, 0.04 mol), and ammonium bromide (trace) was heated to reflux for 24 hr. No apparent reaction was observed. The mixture, after cooling, was heated again to

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[9] U. Wannagat, P. Geymeyer, and G. Sehreiner, *Angew. Chem.*, *Int. Ed. Engl.*, **3** (2), 135 (1964).

[10] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p 311.

reflux with a trace amount of lithium nitride. The distillate was periodically removed by means of a Claisen head take-off adapter. The reaction mixture was allowed to reflux for an additional 16 hr, after which time a total of 4.7 g (80%) of diethoxydimethylsilane was collected. From the residue in the flask, only ethoxytriphenylsilane and hexaphenyldisiloxane were isolated.

1-(Ethoxydimethylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane.—A mixture of 3-aminopropyltriethoxysilane (96.5 g, 0.44 mol), hexamethylcyclotrisilazane (32.0 g, 0.15 mol), and ammonium bromide (0.062 g) was heated to reflux for 3 days. The ammonia generated from the reaction was neutralized periodically with standard hydrochloric acid solution (2.02 *N*). In the first 4 hr. 0.40 mol of ammonia was collected and a total of 0.43 mol (100%) was obtained at the end of the reaction. The reaction mixture was first distilled at atmospheric pressure to yield 10.0 g of diethoxydimethylsilane, bp 110° (lit.[10] bp 113–114°), and further identified by its ir spectrum. Vacuum distillation of the remaining substance gave the expected compound (60.0 g, 49%), bp 70–73° (5 mm). Glpc indicated only one component: nmr (neat) δ 0.00 (s, $SiCH_3$), 0.41 (t, $SiCH_2$), 1.04 (t, chain OCH_2CH_3), 1.07 (t, ring OCH_2CH_3), 1.66 (quintet, CH_2CH_2N), 2.85 (t, NCH_2), 3.56 (quartet, chain OCH_2), 3.64 (quartet ring OCH_2)

Anal. Calcd for $C_{11}H_{27}NO_3Si_2$: C, 47.65; H, 9.74; N, 5.05; Si, 20.22; mol wt, 277. Found: C, 48.01, 47.96; H, 9.89, 9.86; N, 4.92, 4.76; Si, 19.59, 19.97; mol wt, 277 (mass spectrometry).

A second fraction was obtained as a viscous liquid (21 g), bp 96–130° (5 mm). Glpc indicated that it was a mixture of a number of compounds. The major component isolated by preparative glpc was identified as 1-(ethoxydimethylsilyl)-2-ethoxy-2-(2′-diethoxy-1′-aza-2′-silacyclopentane)-1-aza-2-silacyclopentane (M): nmr (neat) δ 0.00 (s 6, $SiCH_3$), 0.22–0.57 (m, 4, $SiCH_2$), 0.90–1.18 (t of t, 12-OCH_2CH_3), 1.32–1.75 (m, 4, -CH_2CH_2N), 2.63–2.92 (m, 4 NCH_2), 3.30–3.80 (t of q, 8, OCH_2).

Anal. Calcd for $C_{16}H_{38}N_2O_4Si_3$: C, 47.29; H, 9.36; N, 6.90; Si, 20.68; mol wt, 406. Found: C, 46.92; H, 8.80; N, 6.83; Si, 20.30; mol wt, 406 (mass spectrometry)

In another similar experiment, one component from the mixture, isolated by glpc, was identified as 1-(ethyoxydimethylsiloxydimethylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane, $(C_2H_5O)_2\text{-}\underbrace{SiC_3H_6N}Si(CH_3)_2OSi(CH_3)_2(OC_2H_5)$.

Anal. Calcd for $C_{13}H_{33}NO_4Si_3$: C, 44.44; H, 9.68; N, 3.98; Si 23.93; mol wt, 351. Found: C, 44.33, 44.49; H, 9.51, 9.56; N, 4.77, 4.77; Si, 23.51, 23.28; mol wt, 351 (mass spectrometry).

The higher boiling residue from these reactions was vacuum distilled and analyzed by mass spectrometry, giving the *m/e* peak shown in Table I.

Cyclotri(2-ethoxy-1-aza-2-silacyclopentane). A. From the Reaction of 3-Aminopropyltriethoxysilane and Hexamethylcyclotrisilazane.—A mixture of 3-aminopropyltriethoxysilane (93.0 g, 0.42 mol), hexamethylcyclotrisilazane (31.0 g, 0.14 mol), and lithium nitride (0.53 g, 0.015 mol) was heated under nitrogen to initiate reaction. The ammonia generated from the reaction was periodically neutralized by standard HCl solution to the methyl red end point. In 5 days, 0.43 mol of ammonia was collected. At the end of ammonia generation, the reaction mixture was distilled under nitrogen to remove the diethoxydimethylsilane (58 g, 93.5%), bp 110–115° (lit.[11] bp 113–114°). The residue, upon vacuum distillation, gave 14.0 g (26%) of the expected compound, bp 120–140° (0.05 mm). A sample for analysis was purified by preparative glpc: nmr (neat) δ 0.3–0.7 (t, 2, $SiCH_2$–), 0.8–1.3 (d of t, 3, –CH_3), 1.4–2.1 (m, 2, –CH_2–), 2.5–3.2 (m, 2, –CH_2N), 3.3–4.0 (d of quartet, 2, –OCH_2–).

Anal. Calcd for $C_{15}H_{33}N_3O_3Si_3$: C, 46.51; H, 8.53; N, 10.85; Si, 21.71; mol wt, 387. Found: C, 46.41, 46.04; H, 9.19, 8.81; N, 10.59, 10.56; Si, 21.55, 21.47; mol wt, 387 (mass spectrometry), 384.28, 380.32 (osmometry).

B. From the Reaction of 3-Aminopropyltriethoxysilane and Lithium Nitride.—Into 3-aminopropyltriethoxysilane (151.0 g, 0.68 mol) warmed to about 50° in a three-necked flask equipped with mechanical stirrer, condenser, and nitrogen inlet and outlet tubes, was added slowly 14.3 g (0.41 mol) of lithium nitride. Reaction took place with generation of heat and ammonia (not collected). From time to time the external heat source had to be removed to ensure a smooth reaction. After complete addition, the reaction mixture was heated to reflux for 2 hr, then cooled to room temperature. The lithium ethoxide was precipitated by addition of 250 ml of xylene and removed by filtration under nitrogen. The filtrate was distilled at atmospheric pressure to remove the solvent. Vacuum distillation gave 28.0 g of the desired compound, bp 115–138° (0.05 mm). Redistillation under vacuum gave 24.0 g (30%) of pure sample. The molecular weight [387 (mass spectrometry)], ir spectrum, and glpc retention time were identical with those of the sample obtained from reaction A.

Condensation Reaction of 1-(Ethoxydimethylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane and Lithium Nitride.—1-(Ethoxydimethylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane (29 g) and lithium nitride (0.0050 g) were heated together under nitrogen overnight. The reaction mixture, after cooling to room temperature, was vacuum distilled. There was obtained 14.2 g of starting material and a small amount of trimer D, identified by its glpc retention time, which was identical with that of an authentic sample.

Alcoholysis of Trimer D.—A mixture of anhydrous ethanol (50 ml) and a few drops of benzene was distilled under nitrogen until the distillation temperature reached 78°. After the alcohol was cooled to room temperature, trimer D (11.0 g) was added and the reaction mixture was heated to reflux for 10 hr. Upon vacuum distillation of the mixture 4.8 g (25%) of 3-aminopropyltriethoxysilane was obtained.

In another similar experiment, a small piece of lithium was added to the alcohol before the addition of 12.5 g of trimer D. Upon refluxing the mixture of 1 hr and vacuum distillation there was obtained 17.0 g (79%) of pure 3-aminopropyltriethoxysilane whose identity was confirmed by its ir spectrum and glpc retention time.

Arylation of Trimer D.—Into a mixture of trimer D (20.6 g, 0.05 mol), 250 ml of anhydrous diethyl ether, and shredded lithium (2.24 g, 0.32 g-atom) was added slowly an excess of bromobenzene (35.0 g). The reaction took place with generation of heat and proceeded smoothly during the addition (3 hr). Lithium salts were precipitated by addition of 200 ml of benzene and removed by filtration under nitrogen. After removal of the benzene, the filtrate was taken up in 100 ml of petroleum ether (bp 30–60°) and cooled. There was obtained 13.7 g of cyclotri(2-phenyl-1-aza-2-silacyclopentane), mp 129–131°. Concentration of the mother liquid gave an additional 1.8 g of the compound for a total yield of 64%. Upon recrystallization from hexane an analytical sample, mp 133°, was obtained: nmr ($CDCl_3$) δ 0.5–1.3 (m, 2, $SiCH_2$–), 1.4–2.2 (m, 2, $SiCH_2CH_2$–), 2.4–3.6 (m, 2, NCH_2), 6.9–8 (m, 5, SiC_6H_5).

Anal. Calcd for $C_{27}H_{33}N_3Si_3$: C, 67.08; H, 6.83; N, 8.70; Si, 17.39; mol wt, 483. Found: C, 67.20, 67.03; H, 6.76, 6.86; N, 8.88, 8.90; Si, 17.31, 17.29; mol wt, 483 (mass spectrometry).

Alcoholoysis of Cyclotri(2-phenyl-1-aza-2-silacyclopentane).—Cyclotri(2-phenyl-1-aza-2-silacyclopentane) (5.09 g) was refluxed in excess anhydrous ethanol under nitrogen for 24 hr. After removal of excess alcohol by distillation the residue was vacuum distilled. A fraction (5.7 g) which distilled over at 110° (2 mm) was found by glpc to exhibit three peaks: a small one for a low-boiling substance, a broad shoulder, and a large major peak, the latter two overlapping. Repeated glpc did not provide any improvement in the resolution: nmr (neat) δ 0.6–1.8 (m, 9.4, $SiCH_2CH_2$–, –NH_2, and –CH_3), 2.62 (t, 2, –CH_2N), 3.87 [q, 2.7 (theoretical, 4, –OCH_2–), 7–7.9 (m, 5, C_6H_5).

Anal. Calcd for $C_{13}H_{23}NO_2Si$: C, 61.66; H, 9.09; N, 5.53; Si, 11.06; mol wt, 253. Found: C, 61.43, 61.52; H, 8.70, 8.96; N, 5.53, 5.53; Si, 12.12, 11.96; mol wt, 265.4, 268.5 (osmometry); *m/e* 253 (weak), 207 (strong).

The liquid product was hydrolyzed in a mixed solvent (benzene, ethyl alcohol, and ammonium hydroxide). After removal of the solvent by distillation, a transparent gluelike substance was obtained.

The nmr spectrum of the substance had four broad peaks [phenyl H(5) and three methylene H(2:2:2)] and a sharp peak for amino-H which corresponded to the structure of 3-aminopropylphenylpolysiloxane, $[NH_2C_3H_6(C_6H_5)SiO]_n$.

Anal. Calcd for $(C_9H_{13}NOSi)_n$: C, 60.34; H, 7.26; N, 7.82; Si, 15.64. Found: C, 59.36, 59.43; H, 7.11, 6.93; N, 8.02, 8.13; Si, 15.42, 15.53.

Alkylation of Trimer D.—1-Bromoethane instead of bromobenzene was used in the above reaction (trimer D, 14 g, 0.036 mol). After the removal of lithium salts, the filtrate was concentrated and vacuum distilled. A fraction, 5.5 g (45%), distilled at 136–156° (0.1 mm) and was shown by glpc to be a pure sample of the desired compound: nmr (neat) δ 0.3–1.2 (m, 7, C_2H_5-$SiCH_2$–), 1.4–2.1 (m, 2, -CH_2–), 2.6–3.2 (m, 2, NCH_2–).

Anal. Calcd for $C_{15}H_{33}N_3Si_3$: C, 53.10; H, 9.73; N, 12.39; Si, 24.77; mol wt, 399. Found: C, 52.97; H, 10.15; N, 11.86; Si, 25.13; mol wt, 339 (mass spectrometry).

Alcoholoysis of Cyclotri(2-ethyl-1-aza-2-silacyclopentane).—Cyclotri(2-ethyl-1-aza-2-silacyclopentane) (0.81 g) was refluxed with excess anhydrous ethanol overnight. A fraction, 0.82 g (56%), distilled at 54° (0.1 mm) and was shown by glpc to be pure 3-aminopropyldiethoxylethylsilane: nmr (neat) δ 0.1–1.6 (m, 10.4, $SiCH_2CH_2$–, $SiCH_2CH_3$, and –NH_2), 0.95, (t, 6, OCH_2CH_3), 2.37 (t, 2, NCH_2–), 3.49 (q, 4, OCH_2).

Anal. Calcd for $C_9H_{23}NO_2Si$: C, 52.68; H, 11.22; N, 6.83; mol wt, 205. Found: C, 53.08, 53.14; H, 11.54, 11.69; N, 6.91, 6.88; mol wt, 205 (mass spectrometry).

Registry No.—1-(Triphenylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane, 32284-27-8; 1-(ethoxydimethylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane, 32284-28-9; trimer D, 32974-82-6; $(C_2H_5O)_2SiC_3H_6NSi(CH_3)_2OSi(CH_3)_2(OC_2H_5)$, 32974-83-7; cyclotri(2-ethoxy-1-aza-2-silacyclopentane, 32974-84-8; cyclotri(2-phenyl-1-aza-2-silacyclopentane, 32974-85-9; 3-aminopropyldiethoxyphenylsilane, 32974-86-0; $[NH_2C_3H_6(C_6H_5)SiO]_n$, 33029-43-5; cyclotri(2-ethyl-1-aza-2-silacyclopentane), 32974-87-1; 3-aminopropyldiethoxylethylsilane, 20723-29-9.

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The Preparation and Reactions of Some 2-Keto-2*H*-pyrido[1,2-*a*]pyrimidines

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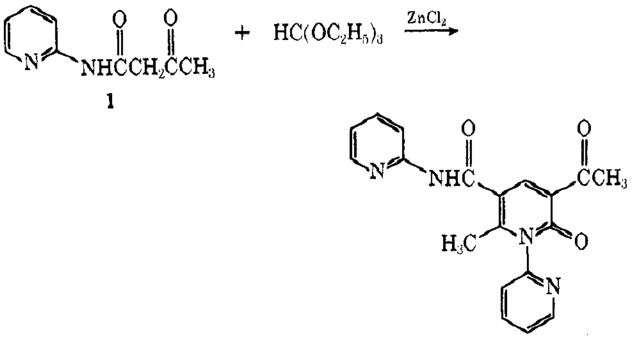
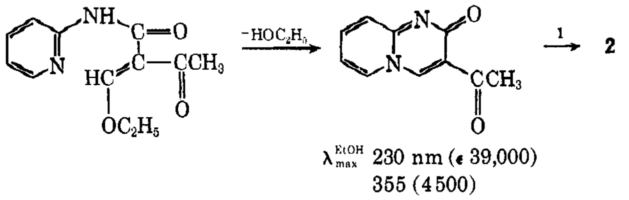
The title compounds are obtained by the reaction of 2-acetoacetylaminopyridines with dimethylformamide dimethyl acetal yielding *N*-(2-pyridyl)-2-acetyl-3-dimethylaminoacrylamides, followed by ring closure with acetic anhydride. The title compounds revert to the starting acrylamides on reaction with dimethylamine; other amines also react with ring opening. The zinc chloride catalyzed reaction with acetoacetamides and the base-catalyzed reaction with acetoacetic esters yield substituted 2-pyridones.

Recently[1] we found that the reaction of 2-acetoacetylaminopyridines (*e.g.*, 1) with triethyl orthoformate and zinc chloride yields substituted 2-pyridones such as 2. To explain this result we proposed a mechanism which involved the formation of a 2-keto-2*H*-pyrido[1,2-*a*]pyrimidine (3) as an intermediate. If 3 really is an intermediate in the formation of products such as 2, it should be quite reactive and form 2 on reaction with 1. The present work was undertaken to prove this point by isolating 3.



1

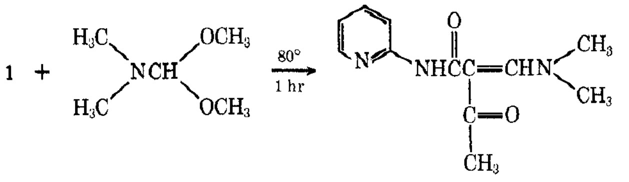
2



λ_{max}^{EtOH} 230 nm (ε 39,000) 355 (4500)

3

Since the reaction of 1 with triethyl orthoformate does not yield the expected ethoxymethylene derivative, the reaction of 1 with dimethylformamided imethyl acetal was used to obtain 4 in 59% yield. Similar results were obtained with other acetoacetylaminopyridines and a carbethoxyacetylaminopyridine (see Table I).



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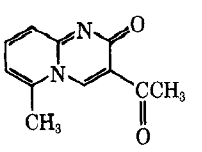
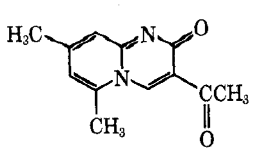
Brief boiling of 4 in acetic anhydride gave an 89% yield of 3 which crystallized out of the hot reaction mixture. A total of five (see Table II) 2-keto-2*H*-pyrido[1,2-*a*]pyrimidines were prepared. Of these, 5 and 6 are of special interest, since they are the product

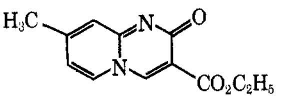


λ_{max}^{EtOH} 226 nm (ε 29,000), 363 (3800)

5



6



λ_{max}^{EtOH} 231 nm (ε 55,000), 341 (5100)

7

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[1] M. C. Seidel, G. C. Van Tuyle, and W. D. Weir, *J. Org. Chem.*, **35**, 1475 (1970).