0.26 g (53%) of **ethyl 2-pyridinecarbamate (5)**. Two recrystallizations from ethanol–water led to a white solid, mp 100.5–102.5° (lit.[10b] mp 102–103°), identical in all respects with the compound prepared from the condensation of ethyl chloroformate and 2-aminopyridine:[10b] ir (KBr) 3.17 (NH) and 5.82 μ (C=O); uv max (95% EtOH) 229 mμ (ε 17,400) and 287 (6650); nmr DMSO-d_6) δ 10.3 (s, 1, NH), 8.35–8.28 (m, 1, C-6 hydrogen), 7.95–7.85 (m, 2, aromatic), 7.30–7.00 (m, 1, aromatic), 4.44–4.05 (q, 2, J = 7 Hz, CH_2CH_3), and 1.40–1.16 (t, 3, J = 7 Hz, CH_3).

Anal. Calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.06; N, 16.85. Found: C, 57.66; H, 6.12; N, 17.00.

Photolysis of Ethyl Azidoformate in the Presence of 1-Phenyl-1,4-Dihydropyridine (6).—1-Phenyl-1,4-dihydropyridine[5] (**6**, 1.28 g, 0.0081 mol) in 90 ml of degassed hexane and 1.76 g (0.015 mol) of ethyl azidoformate under nitrogen were irradiated for 21 hr at 2537 Å with a Hanovia 10-W low-pressure mercury vapor lamp. The solution was filtered and the filtrate was evaporated *in vacuo* to leave a crystalline residue. The residue was dissolved in ethyl ether (Darco), filtered, and pentane was added to the cloud point. Upon cooling there was obtained 0.70 g (36%) of **1-phenyl-2-carbethoxyimino-1,2,3,4-tetrahydropyridine (7)** as white needles (from ether–pentane): mp 95–96°; ir (KBr) 5.93 (C=O) and 6.18 μ (C=N); uv max (95% EtOH) 245 mμ (ε 9500) and 284 (8900); nmr (DMSO-d_6) δ 7.50–7.06 (m, 5, aromatic), 6.40–6.16 (m, 1, J = 7 Hz, NCH=), 5.40–5.10 (m, 1, J = 7.5 Hz, =CH), 4.18–3.84 (q, 2, J = 6.9 Hz, $-CH_2CH_3$), 2.94–2.20 (m, 4, C-3, -4 methylenes), and 1.16 (t, 3, J = 6.9 Hz, CH_3); mass spectrum (70 eV) m/e 244.

Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47; mol wt, 244. Found: C, 68.84; H, 6.89; N, 11.80; mol wt, 232.

Reaction of 1 with *p*-Toluenesulfonyl Isocyanate.—A solution of 1.78 g (0.012 mol) of **1** in 200 ml of degassed anhydrous ethyl ether was brought to 0° under nitrogen. To this mixture was added slowly (45 min) 4.64 g (0.024 mol) of *p*-toluenesulfonyl isocyanate in 50 ml of anhydrous ethyl ether (degassed). Shortly after the start of the addition of the isocyanate, a solid appeared. The mixture was stirred at 0° for 3 hr, after which an unidentified solid (2.1 g) was filtered. Pentane was added to the filtrate and an additional 1.5 g of the same material was filtered. The filtrate was cooled to −20° and then filtered to yield 1.0 g of **N-*p*-toluenesulfonyl-1-trimethylsilyl-1,4-dihydronicotinamide (8)** (22%). One recrystallization (Darco) from anhydrous ethyl ether–pentane gave **8** as yellow plates: mp 123.5–125°; ir (KBr) 3.12 μ (NH), 6.00 (C=O), 7.52, 8.63 (SO_2), 7.95 (Si–CH_3) and 11.80 (Si–C); uv max (95% EtOH) 224 mμ (ε 29,500) and 355 (12,500); nmr ($CDCl_3$) δ 8.39–8.32 (m, 1, NH), 8.09–7.25 (A_2B_2 pattern, 4, J = 8.7 Hz, aromatic), 7.17 (d, 1, J = 2 Hz, C-2 vinyl), 5.90–5.57 (m, 1, J = 2 Hz, C-6 vinyl), 4.93–4.63 (m, 1, J = 3 Hz, C-5 vinyl), 3.12–2.98 (d, 2, J = 3 Hz, CH_2), 2.44 (s, 3, *p*-CH_3), and 0.18 (s, 9, CH_3).

Anal. Calcd for $C_{16}H_{22}N_2O_3SSi$: C, 54.83; H, 6.33; N, 7.99; mol wt, 350. Found: C, 54.82; H, 6.24; N, 8.26; mol wt, 350.

Na–Hg Reduction of 1-Benzylpyridinium Chloride (9).—To a solution of 11.4 g (0.055 mole) of **9**[19] in 1 l. of degassed water was added 120 g (0.026 mol) of 5% sodium amalgam. The mixture was stirred for 16 hr at ambient temperature under nitrogen. The product separated as a gray solid on continued stirring and was filtered. The residue was dissolved in degassed acetone and the solution was brought to the cloud point with water. Cooling and filtration led to 6.0 g (63%) of **1,1′-dibenzyltetrahydro-4,4′-bipyridyl (10)** as chunky white cubes: mp 86–88° [from acetone–water (Darco)] (lit.[14] no melting point reported); uv max (95% EtOH) 228 mμ (ε 12,500) and 285 (3640); nmr ($CDCl_3$) δ 7.26 (s, 10, aromatic), 5.99–5.83 (d, 4, J = 8 Hz, C-2, -2′, -6, -6′ vinyl), 4.50–4.28 (m, 4, C-3, -3′, -5, -5′ vinyl), 4.13 (s, 4, $CH_2C_6H_5$), and 3.00 (m, 2, C-4, -4′ methine).

Anal. Calcd for $C_{24}H_{24}N_2$: C, 84.67; H, 7.11; mol wt, 340. Found: C, 84.68; H, 7.38; mol wt, 362.

Hydrogenation (PtO_2) of **10** in ethyl acetate at 1 atm for 4.5 hr led to **1,1′-dibenzyl-4,4′-bipiperidyl**, mp 133–134° (from anhydrous ethyl ether), lit.[15] mp 133°.

$NaBH_4$ Reduction of 9.—To a solution of 13.8 g (0.25 mol) of KOH in 1 l. of degassed water was added 25.2 g (0.12 mol) of **9**. To this mixture was added 1.67 g (0.044 mol) of $NaBH_4$ in 50 ml of water and the whole was stirred for 16 hr at room temperature under nitrogen. The aqueous solution was extracted with eight 100-ml portions of ethyl ether. The ether extracts were combined, dried ($MgSO_4$), and filtered, and the solvent was removed *in vacuo*. The residue was distilled at 78–84° (0.25 mm) to yield 10.7 g (51%) of a colorless (two-component by vpc) liquid. Chromatography over a 20 ft × 0.375 in. 20% Silicone rubber on 60–80 Chromosorb W column (column temperature 150°, He flow 30 cc min^{-1}) separated the larger component, bp 69–70° (0.2 mm), which was identical with the known **1-benzyl-1,2,5,6-tetrahydropyridine (14)** [lit.[16] bp 68° (0.1 mm); 96° (5 mm)]; uv max (95% EtOH) 251 mμ (ε 300), 257 (335), and 263 (332); nmr ($CDCl_3$) δ 7.23 (s, 5, aromatic), 5.73–5.50 (m, 2, CH), 3.54 (s, 2, $-CH_2C_6H_5$), 3.03–2.80 (m, 2, C-2 methylene), 2.68–2.41 (m, 2, C-6 methylene), and 2.36–2.00 (m, 2, C-5 methylene).

Anal. Calcd for $C_{12}H_{15}N$: C, 83.18; H, 8.57. Found: C, 83.01; H, 8.57.

Hydrogenation (5% Pd–C) of the initial mixture (3 ml, 0.016 mol) obtained from the $NaBH_4$ reduction of **9** in 50 ml of absolute ethanol at 1 atm gave 1.6 g (58%) of **1-benzylpiperidine (15)**, bp 120–122 (13 mm) [lit.[16] bp 110° (6 mm)]; nmr ($CDCl_3$) δ 7.29 (s, 5, aromatic), 3.41 (s, 2, $-CH_2C_6H_5$), 2.50–2.24 (m, 4, C-2, -6 methylenes), and 1.66–1.40 (m, 6, C-3, -4, -5 methylenes).

Na–Hg Reduction of 1-Phenylpyridinium Chloride (12).—The procedure of Saunders and Gold[5] was followed except that 5% sodium amalgam was used and the work-up of Karrer[13] was followed. To a solution of 10.0 g (0.055 mol) of **12** dissolved in 1 l. of degassed water was added 240 g (0.53 mol) of 5% sodium amalgam. The solution was stirred for 16 hr at room temperature under nitrogen. The precipitated solid was filtered and dissolved in degassed acetone. The acetone solution was brought to the cloud point with water and cooled. Filtration of the resulting solid gave 0.60 g (7%) of **1,1′-diphenyltetrahydro-4,4′-bipyridyl (13)** as silvery plates: mp 124–126° (from acetone–water; Darco) (lit.[20] mp 136°); uv max (95% EtOH) 291 mμ (ε 38,800); nmr ($CDCl_3$) δ 7.55–6.95 (m, 10 aromatic), 6.69–6.55 (d, 4, J = 8 Hz, C-2, -2′, -6, -6′ vinyl), 4.90–4.60 (m, 4, C-3, -3′, -5, -5′ vinyl), and 3.16 (m, 2, C-4, -4′ methine).

Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; mol wt, 312. Found: C, 84.46; H, 6.60; mol wt, 309.

Additional water was added to the filtrate and the aqueous solution was extracted with ethyl ether. The ether extracts were dried (Na_2SO_4), filtered, and evaporated *in vacuo*. Recrystallization (Darco) of the residue from methanol gave 1.28 g (15%) of **6** identical with that previously reported.[5]

Registry No.—Ethyl azidoformate, 817-87-8; *p*-tosyl isocyanate, 4083-64-1; **1**, 3337-18-6; **3a**, 21471-13-6; **3b**, 21471-14-7; **4a**, 21471-15-8; **4b**, 21471-16-9; **7**, 21471-17-0; **8**, 21471-18-1; **9**, 2876-13-3; **10**, 16947-42-5; **12**, 13958-90-2.

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Azabicyclic Alcohols. VI. Stereospecific Synthesis of the 1-Azabicylo[2.2.1]heptan-3-ol Epimers[1]

DOUGLAS O. SPRY AND HERBERT S. AARON

Chemical Research Laboratory, Edgewood Arsenal, Maryland 21010

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There are three isomeric azabicyclo[2.2.1]heptane ring systems, depending upon the position of the nitrogen atom. Recently, stereochemical studies in the 2- and 7-aza series were described.[2] In the 1-aza series,

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only the unsubstituted[3] or alkyl[4]-substituted parent are known, and no member bearing a functional substituent has been reported. We now report a new synthetic entree into this system, including a stereospecific synthesis of its *exo* and *endo* 3-hydroxy epimers (**4** and **6**, respectively).

Catalytic hydrogenation of 2,3-dioxo-4-carbethoxypiperidine[5] (**1**) gave, stereospecifically, *cis*-3-hydroxy-4-carbethoxypiperidone-2 (**2**). The observed stereospecificity and assigned stereochemistry of this reduction product are due to the fact that **1** actually exists (from uv and ir spectra) as the enol **1a**, hydrogenation of which would be expected to occur by a *cis* addition of hydrogen to the double bond.[6] Hydride reduction of **2** gave *cis*-3-hydroxy-4-(hydroxymethyl)piperidine (**3**), without affecting, of course, the existing stereochemistry of the system.[7] The conversion of **1a** into **3** was performed in a two-step sequence, because a direct reduction of **1a** with lithium aluminum hydride led to 3-hydroxy-4-methylenepiperidine. This result appears to be typical of β-keto ester systems.[8]

The diol (**3**) was cyclodehydrated on activated alumina in good yield to *exo*-1-azabicyclo[2.2.1]heptan-3-ol (**4**), the configuration of which follows directly from the *cis* stereochemistry of **3**. None of the epimeric *endo* alcohol (**6**) could be detected (glpc) in the product. A control established that the *endo* alcohol (obtained below) is stable under the reaction conditions, hence would have been present had it been formed. These results are offered as proof of the stereochemical purity of the intermediates **2** and **3**.

A structure proof of the azabicyclic ring system was obtained by oxidation of **4** to the corresponding ketone **5**, which was hydrogenolyzed to 1-azabicyclo[2.2.1]-heptane (**7**), identical (ir, glpc, picrate) with that obtained as reported[3b] from 4-(bromomethyl)piperidine. In addition, **7** was also prepared by the cyclodehydration of 4-(hydroxymethyl)piperidine (**8**). See Scheme I.

The *endo*-1-azabicyclo[2.2.1]heptan-3-ol (**6**) was obtained by hydrogenation of **5** over platinum in ethanol. None of the *exo* epimer was detected (glpc). These results are in accord with the fact that hydrogenation of norcamphor, the carbocyclic analog of **5**, gives the corresponding *endo* hydroxy isomer.[9a]

The configurational assignments of the epimeric alcohols **4** and **6** are further corroborated by empirical spectral comparisons with the norborneols, their carbocyclic analogs. Thus, the ir spectra show that each *endo* alcohol has a broader O–H stretching absorption band, which occurs at a slightly higher frequency than that of its *exo* epimer, as reported for norborneol systems.[10] The nmr spectra show that the carbinyl proton signal of each *endo* alcohol occurs as a broader band and at a lower field than that of its *exo* epimer.

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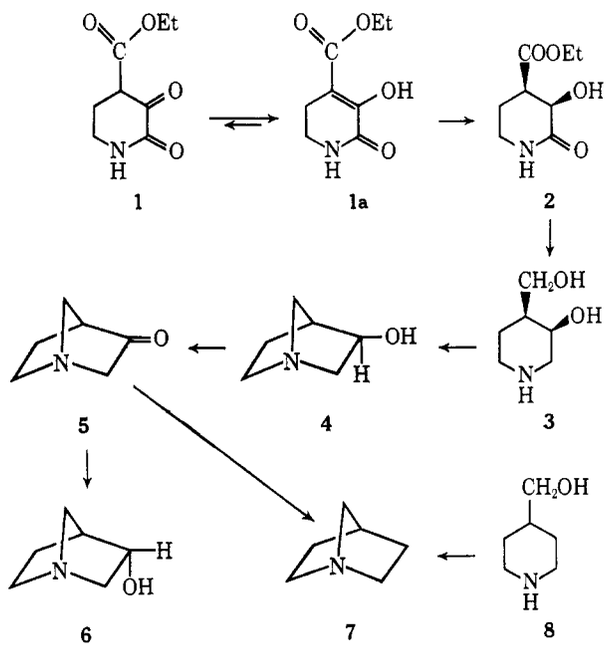
SCHEME I



Experimental Section

***exo*-Norborneol** (Aldrich Chemical Co.), recrystallized from petroleum ether (bp 30–60°), melted at 126–127° (lit.[9b] mp 127–128°). ***endo*-Norborneol** was obtained by reduction[9c] of norcamphor (Aldrich) and melted at 147–148° (petroleum ether) (lit.[9c] mp 149°).

2,3-Dioxo-4-carbethoxypiperidine (**1**) was synthesized[11,12] as described.[5] The compound apparently exists in the enol form **1a**: ir ($CHCl_3$) 1685 (conjugated ester), 1655 (conjugated lactam), and 1605 cm^{-1} (C=C); uv max (H_2O) 240 mμ (ϵ 6800) and 284 mμ (ϵ 5500). The unusual double uv maxima may be due to the presence of *trans* (*e.g.*, **1a**) and *cis* conjugated rotamers of the carbonyl group. Similar structures have been considered for a related system, but without a definitive conclusion regarding conflicting assignments.[13]

***cis*-3-Hydroxy-4-carbethoxypiperidone-2** (**2**).[12]—A solution of **1a** (6.0 g, 32 mmol) in 60 ml of glacial acetic acid was shaken with 0.8 g of 5% rhodium on alumina at 50 psig hydrogen for 1 hr, then filtered, treated with activated charcoal, and evaporated. The residue was recrystallized from benzene to give 4.8 g (80%) of **2**, mp 122–123° (lit.[5] mp 121–122°, from PtO_2 reduction); ir ($CHCl_3$) 1720 (ester) and 1670 cm^{-1} (lactam).

***cis*-3-Hydroxy-4-(hydroxymethyl)piperidine** (**3**).[12]—Compound **2** (9.7 g., 52 mmol) in a thimble of a Soxhlet extractor was slowly dissolved by refluxing tetrahydrofuran (250 ml, freshly distilled from lithium aluminum hydride) into a slurry of lithium aluminum hydride (10 g). The mixture was refluxed with stirring for 48 hr, cooled, and carefully decomposed by the dropwise addition of 20 ml of water. The precipitate was filtered and refluxed with two 150-ml portions of tetrahydrofuran. These were combined with the original filtrate and concentrated to a brown oil, which was distilled at 140° (0.5 μ) to give 4.5 g (66%) of **3**, which crystallized in the condenser to a white solid, mp 126–127°.

Anal. Calcd for $C_6H_{13}NO_2$: C, 54.9; H, 10.0; neut equiv, 131. Found: C, 54.6; H, 9.6; neut equiv, 133.

A picrate was obtained as yellow prisms, mp 131–132° (ethanol–ether).

Anal. Calcd for $C_{12}H_{16}N_4O_9$: C, 40.0; H, 4.5. Found: C, 40.2; H, 4.4.

(11) Prepared by C. A. Feit and coworkers, Regis Chemical Co., under a U. S. Army Research and Development Contract.

(12) Additional quantities were also prepared by Dr. D. A. Scola, P. F. Donovan, and coworkers, Monsanto Research Corp., under a U. S. Army Research and Development Contract.

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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.

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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.

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

TSU-TZU TSAI AND C. J. MARSHALL, JR.

The Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio

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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.

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