Chlorotrimethylsilane, Hexamethyldisilane, and 1,2-Dimethyl-1,1,2,2-tetraphenyldisilane as Oxidizing Agents in the Conversion of Hydrazines to 2-Tetrazenes. Trimethylsilyl Anion as a Leaving Group

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The possibility of the Me_3Si^- species to be a nucleofuge of a compound containing the $NSiMe_3$ group was investigated. Treatment of hydrazines with 1.1 equiv of Me_3SiCl, $Me_3SiSiMe_3$, or $Ph_2MeSiSiMePh_2$ in the presence of 1.0 equiv of potassium hydride gave the corresponding 2-tetrazenes ($R^1R^2NN{=}NNR^1R^2$) in fair to good yields. The hydrazines included 1-methyl-1-phenylhydrazine (**9**), 1-aminopiperidine (**10**), 1-amino-2,6-dimethylpiperidine (**11**), 4-aminomorpholine (**12**), and 1-aminohomopiperidine (**13**). In these reactions, Me_3SiCl, $Me_3SiSiMe_3$, and $Ph_2MeSiSiMePh_2$ acted as oxidizing agents. Results from control experiments supported the proposed mechanism: silylation of hydrazines gave monosilylhydrazines, decomposition of monosilylhydrazines generated aminonitrenes, and dimerization of aminonitrenes afforded 2-tetrazenes. In the decomposition of monosilylhydrazines, Me_3Si^- behaved as a leaving group from the $NSiMe_3$ moiety.

Introduction

Silyl ether **1** can decompose to give ketone **3** under alkaline conditions as shown in Scheme I.[1] We proposed that silyloxy carbanion **2** underwent elimination of Me_3Si^- to give ketone **3** and carried out several experiments in support of this mechanism. To the best of our knowledge, there are no previous examples of Me_3Si^- acting as a leaving group from the $OSiMe_3$ moiety. We intended to explore whether Me_3Si^- can also depart from a nitrogen atom.

1-(Toluenesulfonyl)hydrazines **5**, prepared by tosylation of hydrazines **4**, can decompose to give diazenium cations **6** (Scheme II).[2] Reacting with base, cations **6** are deprotonated to afford aminonitrenes **7**. Aminonitrenes **7** then readily dimerize to provide 2-tetrazenes **8**.[3] The N-2 nitrogen in **5** donates the unshared electron pair to form the π-bond between the N-1 and N-2 nitrogens in **6**. Recognizing the "pushing force" exerted from the N-2 nitrogen,[3,4] we planned to study the fragmentation of monosilylhydrazines, prepared from hydrazines and silylating agents. The Me_3Si group may depart from monosilylhydrazines in the form of Me_3Si^- (cf. p-TolS(O)O$^-$ from **5**). If the fragmentation indeed occurs, aminonitrenes could be generated, and 2-tetrazenes should be the final products.

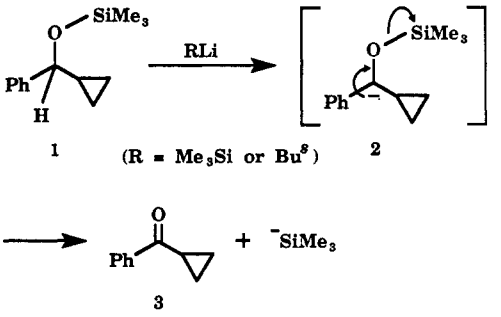
2-Tetrazenes can be made from hydrazines by use of various oxidizing agents: Angeli's salt (Na_2ONNO_2),[5] benzeneseleninic acid,[6,7] quinone,[8,9] Br_2, I_2,[10-13] t-BuOCl,[11] HgO,[11,14-16] MnO_2,[17] $KMnO_4$,[11,15] $KBrO_3$,[12] $Pb(OAc)_4$,[18] etc. 2-Tetrazenes are widely applicable.[19] For example, they serve as chain-transfer agents in vinyl polymerization[20-22] and are a source of free amine radicals.[10,14,21-23] Also, 1,4-dimethyl-1,4-diphenyl-2-tetrazene is an experimental anticancer agent.[24]

This paper describes our findings that Me_3SiCl, $Me_3SiSiMe_3$, and $Ph_2MeSiSiMePh_2$ can separately oxidize 1,1-disubstituted hydrazines to give 2-tetrazenes under alkaline conditions. We will discuss the proposed mechanism, in which the key step involves the release of a silyl group in the anionic form[25] from a monosilylhydrazine.

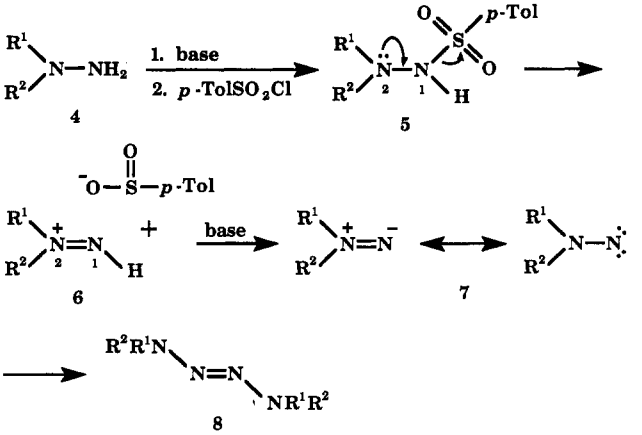
Results

By treating 1-methyl-1-phenylhydrazine (**9**) with 1.0 equiv of potassium hydride in tetrahydrofuran (THF) and then with 1.1 equiv of Me_3SiCl at room temperature for 72 h, we obtained the corresponding 2-tetrazene **14** in 59%

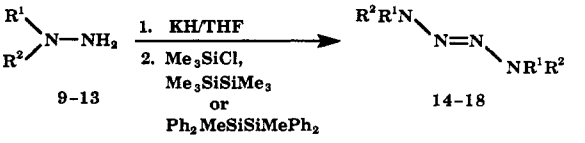
Scheme I



Scheme II



Scheme III



9, 14: R^1 = Ph, R^2 = Me
10, 15: R^1, R^2 = $-(CH_2)_5-$
11, 16: R^1, R^2 = $-CHMeCH_2CH_2CH_2CHMe-$
12, 17: R^1, R^2 = $-CH_2CH_2OCH_2CH_2-$
13, 18: R^1, R^2 = $-(CH_2)_6-$

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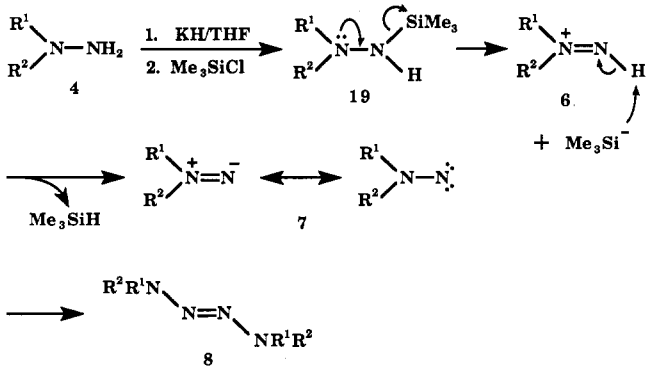
Scheme IV



yield (Scheme III). In the same way, 1-aminopiperidine (**10**) was converted to tetrazene **15** in 32% yield.

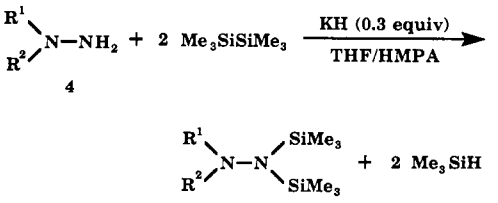
We also employed the same reaction conditions as described above to substrates **9–13** except that Me_3SiCl was replaced by $Me_3SiSiMe_3$ (Scheme III). The corresponding 2-tetrazenes **14–18** were obtained in fair to good yields: **9** → **14** (46%), **10** → **15** (26%), **11** → **16** (52%), **12** → **17** (26%), and **13** → **18** (67%).

Treatment of hydrazine **9** with 1.0 equiv of potassium hydride in THF and then with 1.1 equiv of $Ph_2MeSiSiMePh_2$ gave 2-tetrazene **14** in 95% yield. In the same reaction, the byproduct Ph_2MeSiH was isolated in 90% yield. Methyldiphenylsilane was also obtained in 82% yield when we treated 1-aminopiperidine (**10**) with potassium hydride and $Ph_2MeSiSiMePh_2$ in THF.

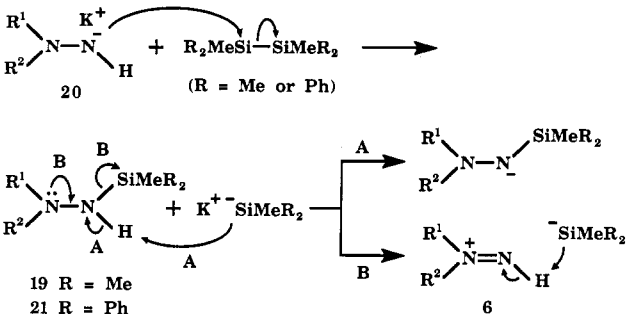
Discussion

Scheme IV depicts our proposed mechanism for the oxidation of 1,1-disubstituted hydrazines (**4**) to 2-tetrazenes (**8**) by use of Me_3SiCl under alkaline conditions. The first step was the monosilylation of hydrazines **4** to **19**. Wannagat and Höfler reported that monosilylhydrazines can be obtained in good yields from Me_3SiCl and excess hydrazines.[26]

Scheme V



Scheme VI



The second step involved the decomposition of monosilylhydrazines **19** in THF at room temperature during prolonged time. When the Me_3Si group transferred from Me_3SiCl to **19**, the silicon atom was electrophilic. When the Me_3Si group left from **19**, the silicon atom bore a negative charge. Thus the oxidation state of the silicon atom decreased by two during the conversion of **4** to **6**. An analogous oxidation–reduction process is the monotosylation of hydrazines **4** with *p*-toluenesulfonyl chloride to give tosylhydrazines **5**, which then decompose to **6** and *p*-TolS(O)O$^-$ (Scheme II).[2] The oxidation state of the sulfur atom also decreases by two. An additional example is the oxidation of hydrazines to 2-tetrazenes with Br_2 or I_2. Halogen atoms in Br_2 and I_2 are reduced.[11,13]

In the third step (i.e., **6** → **7**), Me_3Si^- (liberated from **19**) acted as a base[1] and trapped the acidic NH proton in **6** to provide Me_3SiH and nitrenes **7**. Finally, nitrenes **7** dimerized to give 2-tetrazenes **8**.[3,4]

We found that the yield of **14** from **9** (59%) was higher than that of **15** from **10** (32%) by use of Me_3SiCl. The difference may come from a greater driving force for the generation of the conjugated intermediate **6**, in which R^1 = Ph and R^2 = Me.

Another silicon reagent $Me_3SiSiMe_3$ can also oxidize 1,1-disubstituted hydrazines (**9–13**) to 2-tetrazenes (**14–18**) in THF under alkaline conditions. Analysis of the crude reaction products by GC showed that no disilylated hydrazines were produced. However, the outcome of this reaction changed dramatically when hexamethylphosphoramide (HMPA) was added as the cosolvent: disilylated hydrazines were obtained in excellent yields by treatment of 1,1-disubstituted hydrazines with $Me_3SiSiMe_3$ and potassium hydride in a mixture of THF and HMPA (Scheme V).[27] We discussed the mechanism of the latter reaction in a previous paper.[27]

We rationalized the discrepancy as follows. Hydrazines **20**, generated from hydrazines **4** and potassium hydride,

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can react with $Me_3SiSiMe_3$ to provide monosilylhydrazines **19** and $KSiMe_3$ (Scheme VI). When HMPA was used as the cosolvent, it solvated the K^+ cation.[28] Consequently the "naked" Me_3Si^- became an efficient base to abstract the NH proton in **19** (pathway A in Scheme VI). Conversely, Me_3Si^- generated in the reaction between **20** and $Me_3SiSiMe_3$ in the absence of HMPA would tightly associate with the K^+ cation and was unable to remove the NH proton from **19**. Then monosilylhydrazines **19** were allowed to decompose gradually by pathway B to give cage species containing cations **6** and anion Me_3Si^-. This Me_3Si^- anion (generated in **19** → **6**) did not associate with the K^+ cation and therefore can readily trap the $^+N{=}NH$ proton in its counterpart **6** to give Me_3SiH.

Oxidation of 1,1-disubstituted hydrazines to 2-tetrazenes by Me_3SiCl or $Me_3SiSiMe_3$ gave Me_3SiH as the byproduct. We did not isolate Me_3SiH because of its low normal boiling point (6.7 °C).[29] However, when treating 1-methyl-1-phenylhydrazine (**9**) with $Ph_2MeSiSiMePh_2$, (1.1 equiv, 1.80 mmol) and potassium hydride in THF, we obtained Ph_2MeSiH in 90% yield (1.49 mmol) along with 2-tetrazene **14** (95%). Similarly, treatment of $Ph_2MeSiSiMePh_2$ (1.1 equiv. 2.99 mmol) with 1-aminopiperidine (**10**) in the presence of potassium hydride also gave Ph_2MeSiH in high yield (82%, 2.22 mmol). Results from these experiments supported the proposition of **19** → **7** + Me_3SiH (Scheme IV).[30] Further inspection of the results revealed that a half amount of Ph_2MeSiH was not recovered. The loss might come from the decomposition of Ph_2MeSiK that was generated from $Ph_2MeSiSiMePh_2$ in the conversion of **20** to **21**. This potassium salt was not able to remove the NH proton from **21** because HMPA was absent.

Conclusions

Silicon compounds Me_3SiCl, $Me_3SiSiMe_3$, and $Ph_2MeSiSiMePh_2$ are commonly used as silylating or reducing agents. We found that these compounds can be used as oxidizing agents, which oxidized 1,1-disubstituted hydrazines to give 2-tetrazenes under alkaline conditions. The reaction mechanism was studied; the key step involved the decomposition of monosilylhydrazines to nitrenes and silanes. The results indicated that the Me_3Si group can leave from the $NSiMe_3$ moiety of monosilylhydrazines in the form of Me_3Si^-.

Experimental Section

All reactions were carried out in oven-dried glassware (120 °C) under an atmosphere of nitrogen. Ethyl acetate and hexanes (from Tilley Chemical Co.) and trimethylsilylchloride (from Aldrich Chemical Co.) were dried and distilled over CaH_2. Tetrahydrofuran (from J. T. Baker Chemical Co.) was freshly distilled from Na and benzophenone. Other commercially available chemicals were used directly as received. Potassium hydride (KH, 35%, dispersion in mineral oil) and all hydrazines were purchased from Aldrich Chemical Co. Hexamethyldisilane and 1,2-dimethyl-1,1,2,2-tetraphenyldisilane were purchased from Petrarch Systems. Melting points were obtained with a Büchi 510 melting point apparatus and are not corrected. Analytical TLC was performed on precoated plates purchased from Analtech Inc. (silica gel GHLF). Visualization of spots on TLC plates was made by use of UV light and/or 2.5% phosphomolybdic acid in ethanol with heating. Mixtures of ethyl acetate and hexanes were used as eluants. Analyses by GC were performed on a Hewlett-Packard 5794A instrument equipped with a 12.5-m cross-linked Methylsilicone gum capillary column (0.2-mm i.d.). Purification by gravity column chromatography was carried out by use of EM Reagents silica gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM). Separations by radial thin-layer chromatography were performed on a Model 7924T Chromatotron from Harrison Research. The plates were coated with EM Reagents silica gel 60 PF_{254} containing gypsum. Infrared (IR) spectra were measured on a Perkin–Elmer 599B or 710B spectrophotometer. The wavenumbers reported are referenced to the polystyrene 1601-cm^{-1} absorption. Proton NMR spectra were obtained on a Varian CFT-20 spectrometer with chloroform-*d* as solvent and tetramethylsilane as an internal standard. Proton NMR multiplicities are recorded by use of the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; *J*, coupling constant (hertz). High-resolution mass spectra were obtained by means of a VG Analytical 70-S mass spectrometer.

1,4-Dimethyl-1,4-diphenyl-2-tetrazene (14).[14,31] **Method 1.** Potassium hydride (35% in mineral oil, 190 mg, 1.66 mmol, 1.0 equiv) was added to a dry, one-necked, round-bottomed flask equipped with a stirring bar and a rubber septum and was washed with hexanes (3 × 5 mL). Hexanes were removed to give KH as a white powder. Tetrahydrofuran (8.0 mL) and 1-methyl-1-phenylhydrazine (201 mg, 1.64 mmol, 1.0 equiv) were injected into the flask at 0 °C under an atmosphere of nitrogen. After the suspension was warmed to room temperature and stirred for 1 h, Me_3SiCl (197 mg, 1.81 mmol, 1.1 equiv) was added into the reaction flask. The brown solution was stirred at room temperature for 72 h. Then the reaction was quenched with water (2 mL), and the solution was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and filtered through Celite and silica gel. The crude product was then purified with a Chromatotron (1-mm plate; 10% EtOAc in hexanes as eluant). The desired product **14** was obtained as a yellow-orange oil in 59% yield (117 mg, 0.49 mmol): TLC R_f 0.48 (20% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 70 °C, duration 2.00 min; increment rate 15 °C/min; final temperature 250 °C) t_R 3.49 min; ^1H NMR ($CDCl_3$) δ 2.83 (m, 6 H, 2 CH_3), 6.54–6.78 (m, 5 H, C_6H_5), 7.18–7.48 (m, 5 H, C_6H_5); IR (neat) 3421, 3049, 3033, 2996, 2946, 2921, 2896, 2831, 1621, 1517, 1489, 1456, 1338, 1286, 1227, 1205, 1177, 1096, 1052, 1017, 978, 896, 776, 721 cm^{-1}; exact mass calcd for $C_{14}H_{16}N_4$ 240.1375, found (70 eV) 240.1379.

Method 2. The procedure described in method 1 was followed. The reagents added in the reaction flask included KH (35% in mineral oil, 189 mg, 1.65 mmol, 1.0 equiv), 1-methyl-1-phenylhydrazine (201 mg, 1.65 mmol, 1.0 equiv), $Me_3SiSiMe_3$ (266 mg, 1.82 mmol, 1.1 equiv), and THF (8.0 mL). The desired product **14** was obtained as a yellow-orange oil in 46% yield (125 mg, 0.52 mmol); its physical properties and spectral data are identical with those listed above.

Method 3. The procedure described in method 1 was followed. The reagents added in the reaction flask included KH (35% in mineral oil, 187 mg, 1.63 mmol, 0.99 equiv), 1-methyl-1-phenylhydrazine (202 mg, 1.65 mmol, 1.0 equiv), $Ph_2MeSiSiMePh_2$ (716 mg, 1.80 mmol, 1.1 equiv), and THF (8.0 mL). The desired product **14** was obtained as a yellow-orange oil in 95% yield (188 mg, 0.78 mmol); its physical properties and spectral data are listed above.

The byproduct Ph_2MeSiH[32] was isolated as a colorless, irritant liquid in 90% yield (295 mg, 1.49 mmol): TLC R_f 0.64 (10% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 250 °C) t_R 4.88 min; ^1H NMR ($CDCl_3$) δ 0.57 (s, 3 H, $SiCH_3$), 7.16–7.57 (m, 10 H, Ar H); Si–H signal was not observed in the NMR spectrum; IR (neat) 3069, 3023 (Ar—H), 2964 (Si—CH_3), 2123 (Si—H), 1954, 1885, 1819, 1763, 1597 (C=C),

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1491, 1432, 1260 (Si—CH_3), 1118, 1056, 1030, 1004, 838, 795, 729, 703 cm^{-1}; exact mass calcd for $C_{13}H_{14}Si$ 198.0865, found (70 eV) 198.0860.

1,1′-Azobispiperidine (15).[17] **Method 1.** Potassium hydride (35% in mineral oil, 310 mg, 2.71 mmol, 1.0 equiv) was added to a dry, one-necked, round-bottomed flask equipped with a stirring bar and a rubber septum and was washed with hexanes (3 × 5 mL). Hexanes were removed to give KH as a white powder. Tetrahydrofuran (14 mL) and 1-aminopiperidine (274 mg, 2.72 mmol, 1.0 equiv) were injected into the flask at 0 °C under an atmosphere of nitrogen. After the suspension was warmed to room temperature and stirred for 1 h, Me_3SiCl (325 mg, 2.99 mmol, 1.1 equiv) was added into the reaction flask. The brown solution was stirred at room temperature for 72 h. Then the reaction was quenched with water (2 mL), and the solution was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered through Celite and silica gel, and concentrated to give a viscous, yellow oil. The oil was then purified with a Chromatotron (1-mm plate; 20% EtOAc in hexanes as eluant). After recrystallization from EtOH, the desired product **15** was obtained as white powder in 32% yield (86 mg, 0.44 mmol): mp 43–44 °C (lit.[17] 44 °C); TLC R_f 0.67 (20% EtOAc in hexane); GC (injector temperature 260 °C; column temperature 130 °C) t_R 7.80 min; ^1H NMR ($CDCl_3$) δ 1.46–1.81 (m, 12 H, 2 $(CH_2)_3$), 3.08–3.21 (m, 8 H, 2 (CH_2NCH_2)); IR (CCl_4) 2933, 2853, 2806, 1473, 1459, 1451, 1368, 1275, 1164, 1084, 1070, 987, 928, 869 cm^{-1}; exact mass calcd for $C_{10}H_{20}N_4$ 196.1688, found (70 eV) 196.1691.

Method 2. The procedure described in method 1 was followed. The reagents added in the reaction flask included KH (35% in mineral oil, 312 mg, 2.72 mmol, 1.0 equiv), 1-aminopiperidine (273 mg, 2.72 mmol, 1.0 equiv), $Me_3SiSiMe_3$ (438 mg, 2.99 mmol, 1.1 equiv), and THF (14 mL). The desired product **15** was a white powder in 26% yield (69 mg, 0.35 mmol); its physical properties and spectral data are the same as those listed above.

Method 3. The procedure described in method 1 was followed. The reagents added in the reaction flask included KH (35% in mineral oil, 315 mg, 2.75 mmol, 1.0 equiv), 1-aminopiperidine (98%, 275 mg, 2.72 mmol, 1.0 equiv), $Ph_2MeSiSiMePh_2$ (1.181 g, 2.99 mmol, 1.1 equiv), and THF (14 mL). The desired product Ph_2MeSiH[32] was isolated as a colorless, irritant liquid in 82% yield (440 mg, 2.22 mmol); its physical properties and spectral data are the same as those listed in method 3 in the preparation of **14**.

1,1′-Azobis(2,6-dimethylpiperidine) (16).[6,15] Potassium hydride (35% in mineral oil, 140 mg, 1.22 mmol, 1.0 equiv) was added to a dry, one-necked, round-bottomed flask equipped with a stirring bar and a rubber septum and was washed with hexanes (3 × 5 mL). Hexanes were removed to give KH as a white powder. Tetrahydrofuran (6.0 mL) and 1-amino-2,6-dimethylpiperidine (156 mg, 1.22 mmol, 1.0 equiv) were injected into the flask at 0 °C under an atmosphere of nitrogen. After the suspension was warmed to room temperature and stirred for 1 h, $Me_3SiSiMe_3$ (196 mg, 1.34 mmol, 1.1 equiv) was added into the reaction flask. The brown solution was stirred at room temperature for 72 h. Then the reaction was quenched with water (2 mL), and the solution was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered through Celite, and concentrated to a green oil. The oil was then purified by Chromatotron (1-mm plate; 30% EtOAc in hexanes as eluant). The desired diastereomers **16** were obtained as a solid in 52% yield (80 mg, 0.32 mmol): TLC R_f 0.34 (30% EtOAc in hexanes); ^1H NMR ($CDCl_3$) δ 1.05 (d, J = 6.5 Hz, 12 H, 4 CH_3), 1.30–1.95 (m, 12 H, 2 $(CH_2)_3$), 3.52 (m, 4 H, 4 CH); IR (CCl_4) 2966, 2931, 1451, 1374, 1320, 1283, 1212, 1112, 1036 cm^{-1}; exact mass calcd for $C_{14}H_{28}N_4$ 252.2314, found (70 eV) 252.2315.

4,4′-Azobismorpholine (17).[5,11,17] Potassium hydride (35% in mineral oil, 353 mg, 3.08 mmol, 1.0 equiv) was added to a dry, one-necked, round-bottomed flask equipped with a stirring bar and a rubber septum and was washed with hexanes (3 × 5 mL). Hexanes were removed to give KH as a white powder. Tetrahydrofuran (15 mL) and 4-aminomorpholine (315 mg, 3.08 mmol, 1.0 equiv) were injected into the flask at 0 °C under an atmosphere of nitrogen. After the suspension was warmed to room temperature and stirred 1 h, $Me_3SiSiMe_3$ (496 mg, 3.39 mmol, 1.1 equiv) was added into the reaction flask. The light green solution was stirred at room temperatures for 72 h. Then the reaction was quenched with water (2 mL), and the solution was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered through Celite, and concentrated to give a white solid. The solid was then purified by a silica gel gravity column chromatography (40% EtOAc in hexanes as eluant). The desired product **17** was obtained as a white powderlike solid in 26% yield (81 mg, 0.40 mmol): mp 154–155 °C (lit.[17] mp 157 °C); TLC R_f 0.29 (20% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 130 °C) t_R 7.79 min; ^1H NMR ($CDCl_3$) δ 3.13–3.25 (m, 8 H, 2 (CH_2NCH_2)), 3.76–3.88 (m, 8 H, 2 (CH_2OCH_2)); IR (CCl_4) 2953, 2902, 2881, 2823, 1445, 1268, 1113, 1085, 987, 860 cm^{-1}; exact mass calcd for $C_8H_{16}N_4O_2$ 200.1273, found (70 eV) 200.1272.

1,1′-Azobis(hexahydro-1*H*-azepine) (18).[16,17] Potassium hydride (35% in mineral oil, 188 mg, 1.64 mmol, 1.0 equiv) was added to a dry, one-necked, round-bottomed flask equipped with a stirring bar and a rubber septum and was washed with hexanes (3 × 5 mL). Hexanes were removed to give KH as a white powder. Tetrahydrofuran (8.0 mL) and 1-aminohomopiperidine (187 mg, 1.64 mmol, 1.0 equiv) were injected into the flask at 0 °C under an atmosphere of nitrogen. After the suspension was warmed to room temperature and stirred for 1 h, $Me_3SiSiMe_3$ (264 mg, 1.80 mmol, 1.1 equiv) was added into the reaction flask. The light green solution was stirred at room temperature for 72 h. Then the reaction was quenched with water (2 mL), and the solution was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered through Celite and silica gel, and concentrated to a white solid. The solid was then purified by Chromatotron (1-mm plate; 10% EtOAc in hexanes as eluant). The desired product (**18**) was obtained as a white powderlike solid in 67% yield (123 mg, 0.55 mmol): mp 61–62 °C (lit.[17] mp 62–63 °C); TLC R_f 0.59 (10% EtOAc in hexanes), 0.70 (20% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 130 °C, duration 7.00 min; increment rate 15 °C/min; final temperature 250 °C) t_R 10.95 min; ^1H NMR ($CDCl_3$) δ 1.48–1.82 (m, 16 H, 2 $(CH_2)_4$), 3.38–3.51 (m, 8 H, 2 (CH_2NCH_2)); IR (CCl_4) 2928, 2850, 1072 cm^{-1}; exact mass calcd for $C_{12}H_{24}N_4$ 224.2001, found (70 eV) 224.2002.

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