24 h. The aqueous phase was extracted with CH_2Cl_2 (25 mL × 3), and the combined extracts were evaporated and dried in vacuo. The K_D value ($[CE]_{aq}/[CE]_{org}$) was determined as 0.02.

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Supplementary Material Available: Spectroscopic and analytical data for the new compounds (3 pages). Ordering information is given on any current masthead page.

Silyl-Substituted Cyanoamines as Reagents for Heterocyclic Synthesis

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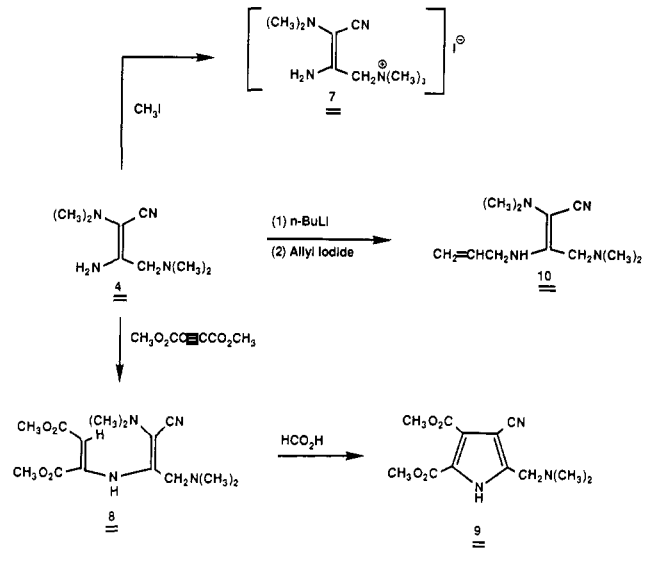
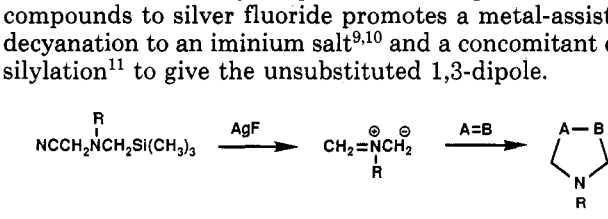
Attempts to silylate the anion derived from several (dialkylamino)acetonitriles with chlorotrimethylsilane gave self-condensation products. Slow addition of chlorotrimethylsilane to (benzylmethylamino)acetonitrile followed by treatment of the resulting ammonium salt with LDA gave the α-silylated cyanoamine in excellent yield. This material on treatment with silver fluoride produced the desilylated cyanoamine rather than an aminocarbene. Treatment of benzyl[(trimethylsilyl)methyl]amino nitrile with silver fluoride in the presence of several trapping agents afforded 1,3-dipolar cycloadducts in good yield. The cycloadditions are believed to proceed via the intermediacy of a cyano-substituted azomethine ylide intermediate. Alkylation of the carbanion derived from (*N*,*N*-dimethylamino)acetonitrile with 5-iodo-1-(trimethylsilyl)-1-pentene proceeded in high yield. The reaction of this material with silver fluoride in aqueous ethanol gave rise to ethyl 6-(trimethylsilyl)-5-hexenoate in good yield without any detectable signs of a cyclized cyanoamine.

In previous papers in this series we outlined a strategy for the synthesis of pyrrolidines wherein the heterocyclic compound was prepared by a 1,3-dipolar cycloaddition of an azomethine ylide.[1] Studies conducted in these[1,2] and other laboratories[3-8] have shown that the desilylation of α-(trimethylsilyl)ammonium salts represent a convenient method for azomethine ylide generation. More recently we described the use of α-cyanomethylaminosilanes as

Scheme I



valuable azomethine ylide precursors.[1] Exposure of these compounds to silver fluoride promotes a metal-assisted decyanation to an iminium salt[9,10] and a concomitant desilylation[11] to give the unsubstituted 1,3-dipole.



From a synthetic standpoint, we were struck by the ease with which this reaction allowed the preparation of a

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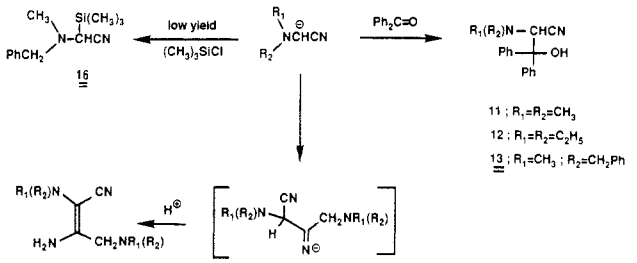
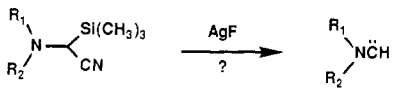
0022-3263/87/1952-2427$01.50/0

Scheme II



reasonably complicated heterocyclic compound. Provided with this stimulus, we decided to embark on studies designed to further develop the chemistry of these silyl-substituted cyanoamines. We were particularly interested in using the desilylation method for the generation of other interesting reactive intermediates. For example, we envisaged that the treatment of α-silylcyanoamines with silver fluoride would serve to generate α-aminocarbenes.

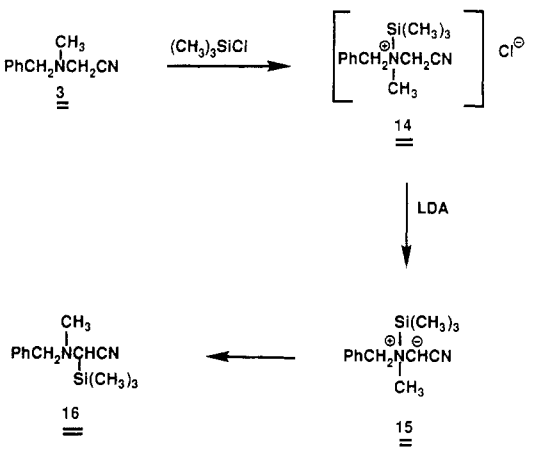


These species are of interest because the strong electron-donating amino group should significantly affect their stability[12] and philicity.[13] Several methods have been reported for the synthesis of aminocarbenes, including the thermal reversion of formal aminocarbene dimers,[14] thermal elimination of an amine or alcohol from an amide acetal or related triheteroatomic substituted methane,[15] deprotonation of amino-stabilized carbocations,[16] the reaction of carbon atoms on amines,[17] the photolysis of a tosylhydrazone salt,[18] and the thermolysis of an aminodiazirine.[19] There is also a report describing the α-elimination of hydrogen cyanide from (dimethylamino)malononitrile.[20] Aminocarbenes have not been generated from the classic diazoalkane carbene precursors.[21]

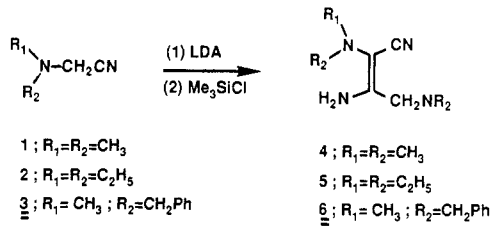
Results and Discussion

We began our study by attempting to silylate the anion derived from several (dialkylamino)acetonitriles. α-Dialkylamino nitriles have received considerable attention

Scheme III



in recent years as acyl anion equivalents.[22-26] These materials readily form carbanions when treated with LDA, and the resulting α-lithioamino nitriles can be quantitatively alkylated.[25] Acid or base cleavage of the bisalkylated amino nitrile is known to produce carbonyl compounds in excellent yield.[22] We found, however, that the anion derived from (dimethylamino)acetonitrile (1) undergoes rapid



self-condensation at −20 °C to give the cyano-substituted enamine **4** in 89% yield. All attempts to isolate an α-silylated amino nitrile failed. The structure of **4** was established on the basis of its spectroscopic and chemical properties (see the Experimental Section). Treatment of **4** with methyl iodide produced the quaternary ammonium salt **7** (Scheme I). Reaction of **4** with dimethyl acetylenedicarboxylate afforded enamide **8**. This material undergoes smooth cyclization to pyrrole **9** when subjected to aqueous formic acid. Finally, reaction of **4** with *n*-butyllithium followed by addition of allyl iodide produced the N-allylated enamine **10**.

In an earlier paper, Stork and co-workers had reported that the self-condensation reaction of (dialkylamino)acetonitriles could be prevented by increasing the steric hindrance around the carbanion center of the heterosubstituted nitrile.[23] Although (*N*,*N*-diethylamino)acetonitrile has been reported to serve as an excellent latent formaldehyde equivalent,[23] we have not been able to isolate the desired silylated cyanoamine using the anion derived from **2**. The only product obtained corresponded to the self-condensation product **5**. A small amount (10%) of the desired silyl-substituted cyanoamine **10** was formed by using (methylbenzylamino)acetonitrile (**3**). Interestingly, the lithium salts of aminoacetonitriles **1**–**3** react readily with benzophenone to give the 1,2-addition products (i.e.,

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(22) Albright, J. D. *Tetrahedron* **1983**, *39*, 3207.
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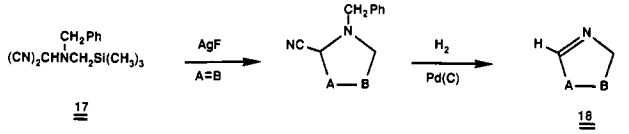
11–13) in good yield without significant formation of the self-condensation products (Scheme II).

We found that the slow addition of chlorotrimethylsilane to (benzylmethylamino)acetonitrile (3) resulted in the formation of silylammonium salt 14. Treatment of a suspension of this salt in THF with LDA led to silylcyanoamine 16 in quantitative yield. No signs of dimer 6 could be detected in the crude reaction mixture. The formation of 16 can be described in terms of the sequence of steps shown in Scheme III. LDA reacts rapidly with the silyl quaternary salt to generate ylide 15, which isomerizes to the final product by migration of the silyl group from nitrogen to carbon. The rearrangement of silicon from carbon to more electronegative elements (O, N, S), is well-known,[27] having been observed under a variety of conditions. With the above system, the driving force for the rearrangement corresponds to the dissipation of charges on the ammonium ylide. We attempted to extend the silylation reaction to other tertiary amines containing simple alkyl groups. Although formation of the silyl salt occurred smoothly, we were unable to induce the silyl rearrangement. More than likely, this failure is related to the difficulty of generating the carbanionic center without the presence of a suitable activating group.

Numerous attempts to trap an aminocarbene derived from silylcyanoamine 16 proved unsuccessful. Treatment of 16 with silver fluoride as well as other Lewis acids and fluoride ion sources failed to give any products attributable to a carbene intermediate. In every case, (*N*-benzyl-*N*-methylamino)acetonitrile (3) was the only product obtained (95% yield). Apparently, the presence of the cyano group is sufficient to promote desilylation prior to iminium ion formation.

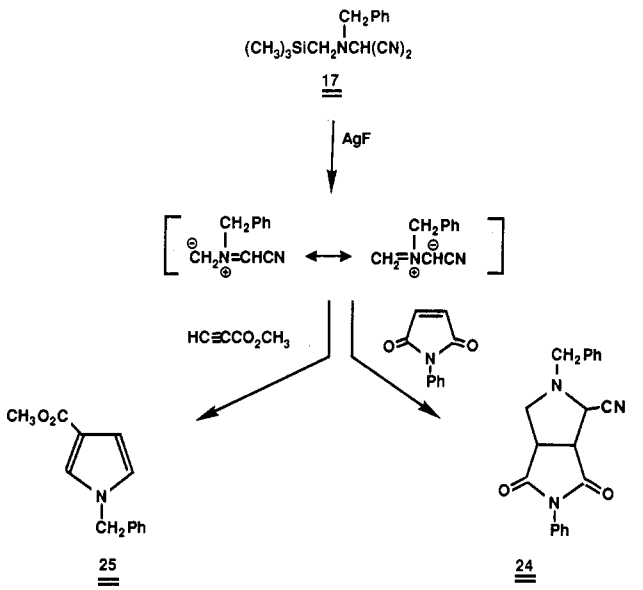
During the course of this work, we also undertook a study of the cycloaddition behavior of [benzyl[(trimethylsilyl)methyl]amino]malononitrile (17), since this



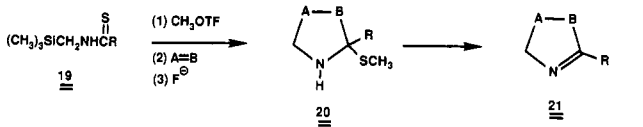
17 18

species can serve as the equivalent of the simplest of all nitrile ylides (i.e., $HC{\equiv}N^{+}CH_2^{-}$). This class of 1,3-dipoles has traditionally been prepared by treatment of imidoyl halides with base[28] or by the photolysis of aryl-substituted azirines.[29-31] More recently, nitrile ylides have been observed to be formed upon photolysis of carbene precursors in nitrile solvents. The nitrile ylides formed in this manner have been trapped by olefinic dipolarophiles.[32-35] A long-standing restriction to the further use of nitrile ylides

Scheme IV

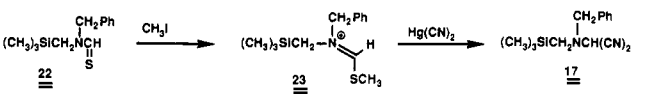


in organic synthesis stems from the fact that simple alkyl-substituted systems are not easily prepared. We have found that (silylamino)malononitrile 17 undergoes smooth dipolar cycloaddition with several dipolarophiles in the presence of silver fluoride. Thus, 17 has the potential of serving as a convenient nitrile ylide precursor, since hydrogenolysis of the benzyl group of the resulting cycloadduct should give rise to the Δ^1-pyrroline ring system.[36] Recent work by Tsuge and co-workers has shown that *N*-(silylmethyl)amidines and thioamides can also serve as nitrile ylide equivalents.[37] Fluoride-induced desilylation of these silyl-substituted thioamides generates azomethine ylides, which undergo successful cycloaddition with a variety of dipolarophiles. The resulting pyrrolidines readily eliminate the thiomethyl group and produce formal nitrile ylide cycloadducts.



19 20 21

[Benzyl[(trimethylsilyl)methyl]amino]malononitrle (17) was prepared by treating thioformamide 22 with methyl



22 23 17

iodide to give the *N*-(silylmethyl)iminium salt 23, which was allowed to react with mercuric cyanide in acetonitrile. In a typical cycloaddition experiment, a solution of 17 and the appropriate dipolarophile was allowed to react in the dark with a slight excess of silver fluoride. Stirring was continued at 60 °C for 24 h. The black precipitate that formed was filtered, and the solvent was removed under reduced pressure to give the 1,3-dipolar cycloadduct. Treatment of 17 with *N*-phenylmaleimide produced a 1:1 mixture of diastereomeric cycloadducts 24 in 80% overall yield (Scheme IV). In the case of methyl propiolate, the initially formed cycloadduct readily lost hydrogen cyanide to give 3-carbomethoxy-*N*-benzylpyrrole (25). Although

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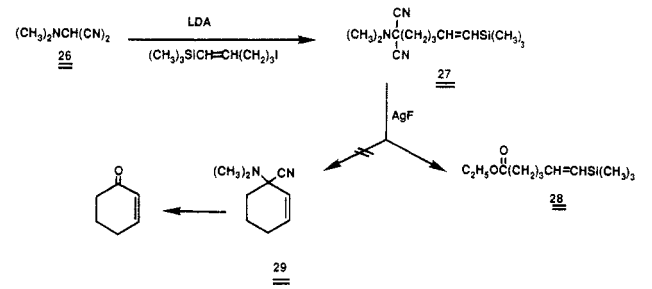
(36) Work is currently underway to develop the hydrogenolysis step for the Δ^1-pyrroline synthesis.

(37) Tsuge, O.; Kanemasa, S.; Yorozu, K.; Ueno, K. *Chem. Lett.* **1985**, 1601; Tsuge, O.; Kanemas, S. *Chem. Lett.* **1985**, 1411; *Heterocycles* **1985**, *23*, 2489; *J. Org. Chem.* **1986**, *51*, 1997.

Scheme V



the cycloaddition reactions occurred in high yield, the conditions are more vigorous than those utilized with simple silylcyanoamines.[2] This can be most reasonably explained by assuming that a significant amount of iminium ion character is developing in the transition state prior to desilylation. The nitrile functionality will destabilize the growing positive charge,[38] and thus, azomethine ylide formation should take place under a more demanding set of conditions.

As a further consequence of our work in this area, we have also studied the base-induced reaction of aminomalononitrile **26**. Protected cyanoamines derived from aldehydes yield carbanions with strong bases such as LDA, and the resulting carbanion undergoes ready alkylation.[22] A similar reaction occurred upon treatment of **26** with LDA, followed by alkylation of the resulting carbanion with various alkyl halides (Scheme V). We were particularly interested in determining whether the 5-silylpentenyl-substituted aminomalononitrile **27** derived from **26** would undergo cyclization upon treatment with silver fluoride. Cationic cyclization is a common method of ring closure in alkaloid synthesis.[39,40] Simple iminium ions, formed in any number of ways, often initiate this process, although acyliminium ions are superior because of their greater reactivity and ease of formation.[41] We envisaged that the cyclization of **27** could give amino nitrile **29**, which, in turn, would afford cyclohexenone upon aqueous hydrolysis. The rationale for choosing **27** was based in part on earlier reports by Overman and co-workers, who found that vinylsilanes can act as efficient terminators for cationic cyclization.[42] Cyanomethylamines are known to function as convenient iminium ion precursors.[9,10] Unfortunately, all of our attempts to obtain a cyclized product from the reaction of **27** with silver fluoride in various nonprotic solvents failed. When the reaction of **27** with AgF was carried out in aqueous ethanol, however, a good yield of ethyl 6-(trimethylsilyl)-5-hexenoate (**28**) could be obtained. It would seem as though polar solvents are essential for iminium ion formation. Once formed, the resulting cation prefers to react with the solvent to give the hydrolyzed ester **28** rather than the cyclized product. It should be noted that **26** is the formal equivalent of ethyl formate anion.

In summary, the silver fluoride induced desilylation of [benzyl[(trimethylsilyl)methyl]amino]malononitrile provides access to a cyano-substituted azomethine ylide, which cycloadds in synthetically useful yields. This reaction is currently being utilized in our laboratory as an alternate method for preparing Δ^1-pyrrolines.

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(41) Speckamp, W. N. *Recl.: J. R. Neth. Chem. Soc.* **1981**, *100*, 345.
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Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer Model 283 infrared spectrometer. Proton NMR spectra were obtained on Varian EM-390 and Nicolet FT-360 spectrometers. ^{13}C NMR spectra were recorded on an IBM 200-MHz spectrometer. Microanalyses were performed at Atlantic Microlabs, Atlanta, GA. Mass spectra were determined with a Finnigan 4000 mass spectrometer at an ionizing voltage of 70 eV.

Reaction of (Dimethylamino)acetonitrile (1) with LDA. To a stirred solution of lithium diisopropylamide prepared from 12.1 g of diisopropylamine and 67 mL of a 1.5 M *n*-butyllithium solution in 100 mL of dry tetrahydrofuran at −20 °C was added dropwise 8.4 g of (dimethylamino)acetonitrile.[43] Within 20 min of stirring, a white precipitate had formed. The reaction mixture was kept at this temperature for 1 h and was allowed to warm to 0 °C for an additional 2 h. To this solution was added 30 mL of a saturated aqueous ammonium chloride solution, and the resulting mixture was extracted with dichloromethane. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure to leave an oil, which was taken up in a small amount of ether. The solution was filtered, and the solvent was removed under reduced pressure to give 7.5 g (89%) of (*Z*)-3-amino-2,4-bis(dimethylamino)-2-butenonitrile (**4**) as an yellow oil, which was distilled at 80 °C (0.3 mm) to give a low-melting solid: mp 33–34 °C; IR 2795, 2205, 1635, 1465, 1395, 1165, 1135, 1045, 870 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.23 (s, 6 H), 2.38 (s, 6 H), 3.07 (s, 2 H), 5.07 (br s, 2 H); UV (acetonitrile) 258 nm (ϵ 13370); MS, *m/e* 168 (M^+), 123, 122, 108, 107, 83. Anal. Calcd for $C_8H_{16}N_4$: C, 57.11; H, 9.59; N, 33.30. Found: C, 56.96; H, 9.66; N, 33.16.

This material was converted to its corresponding ammonium salt by reaction with methyl iodide. To a solution containing 110 mg of (*Z*)-3-amino-2,4-bis(dimethylamino)-2-butenonitrile (**4**) in 2 mL of ether was added 93 mg of methyl iodide. After the mixture was stirred for 12 h, the solid that formed was filtered to give 174 mg (86%) of **7** as a white solid: mp 171–172 °C; IR (KBr) 3380, 3280, 3155, 2200, 1638, 1610, 1450, 1405, 1365, 1205, 1140, 990, 960, 910, 880 cm^{-1}; ^1H NMR (90 MHz, acetone-d_6) δ 2.42 (s, 6 H), 3.3 (br s, 2 H), 3.55 (s, 9 H), 4.76 (s, 2 h). Anal. Calcd for $C_9H_{19}N_4I$: C, 34.85; H, 6.17; N, 18.06. Found: C, 34.56; H, 6.18; N, 17.90.

Preparation of (*Z*)-3-(Allylamino)-2,4-bis(dimethylamino)-2-butenonitrile (10). To a solution containing 0.71 g of (*Z*)-3-amino-2,4-bis(dimethylamino)-2-butenonitrile (**4**) in 10 mL of tetrahydrofuran at 0 °C was added 3.77 mL of a 1.12 M *n*-butyllithium solution in hexane. The mixture was kept at 0 °C for 20 min, and then 0.783 g of allyl iodide in 5 mL of tetrahydrofuran was added. The mixture was kept at −10 °C for 12 h and was then quenched by the addition of 20 mL of water and 10 mL of a 2 N hydrochloric acid solution. The aqueous mixture was extracted with ether, and the ether extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure left a pale yellow oil, which was chromatographed on a silica gel thick-layer plate, using a 2:1 chloroform–ether miture as the eluent. The major fraction isolated contained 0.26 g (30%) of **10** as a pale yellow oil: IR (neat) 3340, 2950, 2200, 1620, 1465, 1160, 1040, 930, 860 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 2.22 (s, 6 H), 2.36 (s, 6 H), 3.06 (s, 2 H), 3.88–4.08 (m, 2 H), 4.98–5.25 (m, 3 H). Anal. Calcd for $C_{11}H_{20}N_4$: C, 63.42; H, 9.68; N, 26.90. Found: C, 63.17; H, 9.54; N, 26.76.

Reaction of (*Z*)-3-Amino-2,4-bis(dimethylamino)-2-butenonitrile (4) with Dimethyl Acetylenedicarboxylate. A solution containing 0.6 g of **4** and 0.51 g of dimethyl acetylenedicarboxylate in 5 mL of ether at 20 °C was stirred for 24 h. The solution was concentrated under reduced pressure to leave behind a clear oil, which was chromatographed on a silica gel thick-layer plate, using 3:1 hexane–ether mixture as the eluent. The major component isolated contained 400 mg (36%) of an yellow solid whose structure was assigned as **8** on the basis of its spectral properties: mp 92–93 °C; IR (KBr) 3200, 2970, 2840, 2800, 2205, 1735, 1685, 1625, 1600, 1465, 1440, 1390, 1295, 1235, 1130, 1035,

(43) Turner, R. A. *J. Am. Chem. Soc.* **1946**, *68*, 1607.

780 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 2.10 (s, 6 H), 2.42 (s, 6 H), 3.22 (s, 2 H), 3.75 (s, 3 H), 3.83 (s, 3 H, 5.60 (s, 1 H), 10.01 (br s, 1 H). Anal. Calcd for $C_{14}H_{22}N_4O_4$: C, 54.18; H, 7.14; N, 18.05. Found: C, 54.11; H, 7.18; N, 18.03.

A solution containing 100 mg of 8 in 2 mL of a 90% formic acid solution was allowed to stand for 48 h at 20 °C. The mixture was the neutralized with a saturated solution of sodium carbonate and extracted with dichloromethane. The combined organic extracts were dried over anhydrous magnesium sulfate and concentrated under reduced pressure to leave behind 62 mg of 2,3-dicarbomethoxy-4-cyano-5-[(dimethylamino)methyl]pyrrole (**9**) as a pale yellow oil: IR (neat) 3320, 2220, 1735, 1670, 1638 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 6 H), 3.22 (s, 3 H), 3.70 (s, 2 H), 3.72 (s, 3 H). Anal. Calcd for $C_{12}H_{15}N_3O_4$: C, 54.33; H, 5.70; H, 15.84. Found: C, 54.19; H, 5.62; N, 15.71.

Reaction of (Dimethylamino)acetonitrile (1) with LDA in the Presence of Benzophenone. To a solution of lithium diisopropylamide in 10 mL of tetrahydrofuran (prepared from 1.21 g of diisopropylamine and 6.7 mL of a 1.5 M *n*-butyllithium solution in hexane at −10 °C) was added dropwise at −60 °C 0.84 g of (dimethylamino)acetonitrile (**1**) in 10 mL of tetrahydrofuran. After the mixture was stirred at −60 °C for 10 min, 1.82 g of benzophenone in 5 mL of tetrahydrofuran was added. The mixture was allowed to warm to room temperature and was quenched with 15 mL of a saturated aqueous ammonium chloride solution. The aqueous phase was extracted with 10 mL of ether, and the combined organic extracts were dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The resulting residue was crystallized from dichloromethane–ether to give 1.06 g (40%) of a white solid. The structure of this material was assigned as 2-(dimethylamino)-3-hydroxy-3,3-diphenylpropionitrile (**11**): mp 140–141 °C; IR (KBr) 3380, 2800, 2265, 1500, 1455, 1395, 1200, 1050, 770, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 2.24 (s, 6 H), 4.22 (s, 1 H), 4.58 (s, 1 H), 7.23–7.78 (m, 10 H). Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.41; H, 6.88; N, 10.47.

Reaction of (Diethylamino)acetonitrile (2) with LDA. To a stirred solution of lithium diisopropylamide in 30 mL of dry tetrahydrofuran prepared from 3.03 g of diisopropylamine and 20.1 mL of a 1.5 M *n*-butyllithium solution in hexane at −15 °C was added dropwise 3.37 g of (diethylamino)acetonitrile[44] in 10 mL of tetrahydrofuran. The mixture was stirred for 2 h at 0 °C and for 1 h at 20 °C. At the end of this time, 10 mL of a saturated ammonium chloride solution was added. The organic phase was separated, dried, and concentrated under reduced pressure to leave an oil, which was taken up in 30 mL of ether. The ether layer was washed with a saturated sodium chloride solution and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude oil was distilled at 80 °C (0.1 mm) to give 2.7 g (80%) of (*Z*)-3-amino-2,4-bis(diethylamino)-2-butenonitrile (**5**) as a yellow oil: IR (neat) 3465, 3345, 2980, 2830, 2200, 1630, 1550, 1455, 1385, 1175, 1095, 1075 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.98 (t, 6 H), 1.03 (t, 6 H), 2.51 (q, 4 H), 2.60 (q, 4 H), 3.33 (s, 2 H), 5.30 (br s, 2 H); MS, *m/e* 224 (M^+), 195, 192, 151, 136, 122, 108, 86 (base). Anal. Calcd for $C_{12}H_{24}N_4$: C, 64.24; H, 10.78; N, 24.98. Found: C, 64.06; H, 10.63; N, 25.02.

Reaction of (Diethylamino)acetonitrile (2) with LDA in the Presence of Benzophenone. To a solution of lithium diisopropylamide in 10 mL of tetrahydrofuran (prepared from 1.11 g of diisopropylamine and 6.7 mL of a 1.5 M *n*-butyllithium solution in hexane at 0 °C) was added dropwise at −70 °C 1.12 g of (diethylamino)acetonitrile (**2**) in 30 mL of tetrahydrofuran. The solution was stirred at −70 °C for 30 min, and then 1.82 g of benzophenone in 10 mL of tetrahydrofuran was added. The mixture was allowed to warm to room temperature and was then quenched by the addition of 15 mL of a saturated aqueous ammonium chloride solution. The aqueous phase was extracted with 10 mL of ether, and the combined organic extracts were dried over anhydrous magnesium sulfate and evaporated under reduced pressure to leave a yellow oil. This material was crystallized from ether–hexane to give 1.33 g (45%) of a white solid. The structure of this material is assigned as 2-(diethylamino)-3-hydroxy-3,3-diphenylpropionitrile (**12**): mp 68–69 °C; IR (KBr) 3410, 2950, 2255, 1500, 1455, 1370, 1185, 1065, 770, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.98 (t, 6 H), 2.11–2.73 (m, 4 H), 4.28 (s, 1 H), 5.06 (br s, 1 H), 7.23–7.90 (m, 10 H). Anal. Calcd for $C_{19}H_{22}N_2$: C, 77.52; H, 7.53; N, 9.51. Found: C, 77.49; H, 7.59; N, 9.46.

Preparation and Reaction of (*N*-Benzyl-*N*-methylamino)acetonitrile (3) with *n*-Butyllithium. To a stirred solution containing 5.0 g of *N*-benzylmethylamine in 60 mL of 1.0 N hydrochloric acid was added 4.76 g of a 37% formaldehyde solution and 6.5 g of potassium cyanide. The reaction mixture was stirred at room temperature for 16 h. At the end of this time, 120 mL of distilled water was added, and the mixture was extracted with ether. The organic layer was washed with water and then a saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to give 6.50 g (100%) of (*N*-benzyl-*N*-methylamino)acetonitrile (**3**) as a clear oil: IR (neat) 3020, 2980, 2805, 2220, 1505, 1455, 1375, 1130, 1040, 1025, 865, 845, 745, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 2.30 (s, 3 H), 3.35 (s, 2 H), 3.55 (s, 2 H), 7.30 (s, 5 H).

To a stirred solution containing 1.00 g of **3** in 5 mL of dry tetrahydrofuran at −78 °C was added 5 mL of a 1.43 M solution of *n*-butyllithium. After the mixture was stirred for 20 min, 1.08 mL of hexamethylphosphoric triamide was added. The mixture was stirred at −78 °C for 2 h and was then allowed to warm to room temperature. The solution was poured into water and extracted with ether. The organic layer was washed with water and dried over magnesium sulfate. Removal of the solvent left a dark residue, which was subjected to silica gel chromatography, using a 4% ethyl acetate–hexane mixture as the eluent. The major fraction isolated contained 800 mg (40%) of a clear oil whose structure was assigned as (*Z*)-3-amino-2,4-bis(benzylmethylamino)crotononitrile (**6**) on the basis of its spectral properties: IR (neat) 3480, 3360, 3015, 2950, 2830, 2180, 1640, 1560, 1500, 1450, 1370, 1140, 1025, 865, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.85 (s, 3 H), 2.40 (s, 3 H), 3.00 (s, 2 H), 3.20 (s, 2 H), 3.60 (s, 2 H), 5.00 (br s, 2 H), 6.90–7.40 (m, 12 H). Anal. Calcd for $C_{20}H_{24}N_4$: C, 74.96; H, 7.55; N, 17.49. Found: C, 74.83; H, 7.51; N, 17.34.

Reaction of (*N*-Benzyl-*N*-methylamino)acetonitrile (3) with Chlorotrimethylsilane and LDA. To a stirred solution containing 11.4 mL of dry diisopropylamine in 30 mL of anhydrous tetrahydrofuran at −78 °C was added 48.9 mL of a 1.66 M solution of *n*-butyllithium in hexane. After the mixture was stirred for 30 min, the resulting LDA solution was added to a suspension of the salt derived from 10.0 g **3** and 10.1 g of chlorotrimethylsilane in 10 mL of dry tetrahydrofuran at −78 °C. The mixture was stirred at this temperature for 2 h and was then allowed to warm to room temperature. The solution was poured into water and extracted with ether. The organic layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was distilled under reduced pressure [bp 135–140 °C (0.5 mm)], and the major fraction corresponding to (methylbenzylamino)(trimethylsilyl)acetonitrile **16** was collected: 14.0 g (96%); IR (neat) 3080, 3050, 2960, 2800, 2220, 2190, 1500, 1455, 1375, 1255, 1130, 1040, 1030, 850, 740, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.20 (s, 9 H), 2.18 (s, 3 H), 3.03 (s, 1 H), 3.60 (AB quartet, J = 13.09 Hz, 2 H), 7.28 (s, 5 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ −3.00, 42.1, 47.2, 63.3, 117, 126, 127, 129, 138; MS, *m/e* 232 (M^+), 160, 134, 118, 114, 100, 92, 91, 83. Anal. Calcd for $C_{13}H_{20}N_2S$: C, 67.24; H, 8.62; N, 12.06. Found: C, 67.25; H, 8.67; N, 12.00.

Preparation of [Benzyl[(trimethylsilyl)methyl]amino]malononitrile (17). A mixture containing 1.93 g of [(trimethylsilyl)methyl]benzylamine and 3.06 g of butyl formate in 50 mL of anhydrous benzene was heated at reflux under a nitrogen atmosphere. After 72 h, the reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The oily residue that remained was taken up in 50 mL of anhydrous toluene. A 2.03 g sample of Lawesson's reagent was added, and the mixture was heated at reflux under a nitrogen atmosphere for 3 h. After the mixture cooled to room temperature, the solvent was removed under reduced pressure, and the resulting residue was subjected to silica gel chromatography using a 7% ethyl acetate–hexane mixture as the eluent. The major fraction isolated contained 1.47 g (62%) of benzyl[(trimethylsilyl)methyl]thioformamide (**22**) as a colorless oil: IR (neat) 2950, 1600,

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1500, 1275, 1120, 850 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.11 (s, 9 H), 3.00 and 3.42 (s, 2 H), 4.62 and 5.08 (s, 2 H), 7.07–7.42 (m, 5 H), 9.27 and 9.33 (s, 1 H). This material was used in the next step without further purification.

A solution containing 422 mg of the above compound and 0.22 mL of methyl iodide in 10 mL of methylene chloride was heated at reflux under a nitrogen atmosphere for 2 h. The solvent was removed under reduced pressure, and the residue was taken up in 10 mL of the acetonitrile. To this mixture was added 449 mg of mercuric cyanide, and the solution was stirred at room temperature for 1.5 h. The reaction mixture was filtered, and the solvent was removed under reduced pressure. The resulting residue was subjected to silica gel chromatography using a 5% ethyl acetate–hexane mixture as the eluent. The major fraction isolated from the column contained 340 mg (74%) of [benzyl[(trimethylsilyl)methyl]amino]malononitrile (**17**) as a clear oil: IR (neat) 2900, 1600, 1495, 1455, 1425, 1370, 1250, 1180, 850, 755, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.18 (s, 9 H), 2.28 (s, 2 H), 3.62 (s, 2 H), 4.47 (s, 1 H), 7.33 (s, 5 H); MS, *m/e* 257 (M^+) 256, 231, 192, 166, 158, 130, 113, 91 (base). Anal. Calcd for $C_{14}H_{19}N_3Si$: C, 65.23; H, 7.44; N, 16.32. Found: C, 65.35; H, 7.46; N, 16.34.

Reaction of [Benzyl[(trimethylsilyl)methyl]amino]malononitrile (17) with Silver Fluoride in the Presence of *N*-Phenylmaleimide. A mixture containing 150 mg of **17**, 82 mg of siliver fluoride, and 100 mg of *N*-phenylmaleimide in 5 mL of anhydrous acetonitrile was heated at 60 °C under a nitrogen atmosphere for 24 h. The reaction mixture was diluted with methylene chloride and was filtered through a pad of Celite. The solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography using a 25% hexane–ether mixture as the eluent. The major fraction isolated from the column contained 138 mg (80%) of a diastereomeric mixture of 4-benzyl-3-cyano-2,6-dioxo-1-phenyl-1,4-diazabicyclo[3.3.0]octane (**24**): ^1H NMR ($CDCl_3$, 360 Mz) δ 2.95 (dd, 1 H, J = 10.8, 7.92 Hz), 3.02 (dd, 1 H, J = 10.08, 7.92 Hz), 3.42–3.73 (m, 4 H), (m, 4 H), 3.89–4.00 (m, 1 H), 4.27 (s, 1 H), 4.32 (d, J = 12.6 Hz, 1 H), 7.26–7.55 (m, 10 H); MS, *m/e* 331 (M^+), 254, 240, 160, 91. Anal. Calcd for $C_{20}H_{17}N_3O_2$: C, 72.49; H, 5.17; N, 12.68. Found: C, 72.36; H, 5.09; N, 12.59.

Reaction of [Benzyl[(trimethylsilyl)methyl]amino]malononitrile (17) with Silver Fluoride in the Presence of Methyl Propiolate. A mixture containing 383 mg of **17**, 207 mg of anhydrous silver fluoride, and 0.26 g of methyl propiolate in 20 mL of anhydrous acetonitrile was heated at reflux under a nitrogen atmosphere. The reaction mixture was diluted with methylene chloride and was filtered through a pad of Celite. Removal of the solvent under reduced pressure left an oily residue, which was subjected to silica gel chromatography using a 15% ethyl acetate–hexane mixture as the eluent. The major fraction isolated from the column contained 220 mg (69%) of 3-carbomethoxy-*N*-benzylpyrrole (**25**): NMR ($CDCl_3$, 90 MHz) δ 3.78 (s, 3 H), 5.03 (s, 2 H), 6.57–6.60 (m, 2 H), 7.03–7.40 (m, 6 H). The structure of this material was unambiguously established by comparison with an authentic sample.[45]

Preparation of (Dimethylamino)[5-(trimethylsilyl)-4-pentenyl]malononitrile (27). To a solution containing 11.7 g of *trans*-1-(trimethylsilyl)-2-(tri-*n*-butylstannyl)ethylene in 75 mL of anhydrous tetrahydrofuran at −78 °C under a nitrogen atmosphere was added 23 mL of a 1.3 M solution of *n*-butyllithium in hexane over a 30-min period. After the additon was complete, the reaction mixture was warmed to −30 °C over a 40-min period. The solution was cooled to −78 °C and 4.71 g of 1-bromo-3-chloropropane was added. After being stirred for 1 h at −78 °C, the reaction mixture was allowed to warm to room temperature and was stirred for another 5 h. After standard workup, the residue was distilled to give 3.97 g (75%) of 5-chloro-1-(trimethylsilyl)-1-pentene as a colorless oil: ^1H NMR (CCl_4, 90 MHz) δ 0.2 (s, 9 H), 1.67–2.33 (m, 4 H), 3.43 (t, 2 H), J = 6.0 Hz), 5.60 (d, 1 H, J = 18 Hz), 5.93 (dt, 1 H, J = 18, 5.25 Hz).

A solution containing 2.62 g of the above compound and 5.55 g of sodium iodide in 25 mL of acetone was heated at reflux for 24 h. After standard workup, the residue was distilled to give 3.66 g (92%) of 5-iodo-1-(trimethylsilyl)-1-pentene as a colorless oil: IR (neat) 2950, 1615, 1430, 1245, 1205, 990, 865, 835, 700 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 0.2 (s, 9 H), 1.78–2.27 (m, 4 H), 3.10 (t, 2 H, J = 6.0 Hz), 5.60 (d, 1 H, J = 18 Hz), 5.93 (dt, 1 H, J = 18, 5.25 Hz).

A lithium diisopropylamide solution was prepared by treating a mixture containing 0.32 mL of dry diisopropylamine in 15 mL of anhydrous tetrahydrofuran at 0 °C with 1.20 mL of a 1.19 M solution of *n*-butyllithium in hexane under a nitrogen atmosphere. After the mixture was stirred for 15 min, 0.33 mL of hexamethylphosphoramide was added. This was followed by the dropwise addition of 0.21 g of (dimethylamino)malononitrile in 0.5 mL of anhydrous tetrahydrofuran. After the mixture was stirred for 1 h, 0.52 g of 5-iodo-1-(trimethylsilyl)-1-pentene in 1 mL of anhydrous tetrahydrofuran was added. The reaction mixture was allowed to warm to room temperature and was then heated at reflux for 6 h. After standard workup, the oily residue that was obtained was subjected to silica gel chromatography using a 2.5% ethyl acetate–hexane mixture as the eluent. The major fraction isolated from the column contained 0.29 g (60%) of (dimethylamino)[5-(trimethylsilyl)-4-pentenyl]malononitrile (**27**) as a colorless oil: IR (neat) 2940, 2885, 2835, 2790, 1620, 1470, 1250, 1050, 1000, 880, 850, 710 cm^{-1}; ^1H NMR (CCl_4) 1.46–2.23 (m, 6 H), 2.33 (s, 6 H), 5.59 (d, 1 H, J = 18.0 Hz), 5.93 (dt, 1 H, J = 18.0, 4.50 Hz). Anal. Calcd for $C_{12}H_{24}N_2Si$: C, 64.23; H, 10.78; N, 12.49. Found: C, 64.05; H, 10.53; N, 12.26.

Reaction of (Dimethylamino)[5-(trimethylsilyl)-4-pentenyl]malononitrile (27) with Silver Nitrate in Ethanol. To a solution containing 42 mg of **27** in 3 mL of anhydrous ethanol under a nitrogen atmosphere was added 57 mg of silver nitrate. After the mixture was stirred in the dark for 18 h, the reaction mixture was filtered and diluted with ether. The ether solution was washed with a saturated sodium bicarbonate solution and a saturated sodium chloride solution and was then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. Flash chromatography of the resulting residue on silica gel using a 3% ethyl acetate–hexane mixture gave 33 mg (91%) of ethyl 6-(trimethylsilyl)-5-hexenoate (**28**) as a colorless oil: IR (neat) 2950, 1730, 1608, 1450, 1370, 1250, 1180, 1000, 850 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 0.02 (s, 9 H), 1.20 (t, 3 H, J = 6.0 Hz), 1.53–2.26 (m, 6 H), 4.17 (q, 2 H, J = 6.0 Hz), 5.57 (d, 1 H, J = 18.0 Hz), 5.97 (dt, 1 H, J = 18.0, 6.0 Hz). Anal. Calcd for $C_{11}H_{22}O_2Si$: C, 61.63; H, 10.35. Found: C, 61.38; H, 10.27.

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