CHE-84-18437). The X-ray structures of compounds 16, 24, and 36 were determined by Dr. Fred Hollander, of the Berkeley College of Chemistry X-Ray Facility.

Supplementary Material Available: X-ray crystallographic data for compounds 16, 24, and 36, including experimental details, general temperature factor expressions, thermal and positional parameters of non-hydrogen atoms, bond lengths, bond angles, and torsional angles (24 pages). Ordering information is given on any current masthead page.

On the Use of *N*-[(Trimethylsilyl)methyl]amino Ethers as Capped Azomethine Ylide Equivalents

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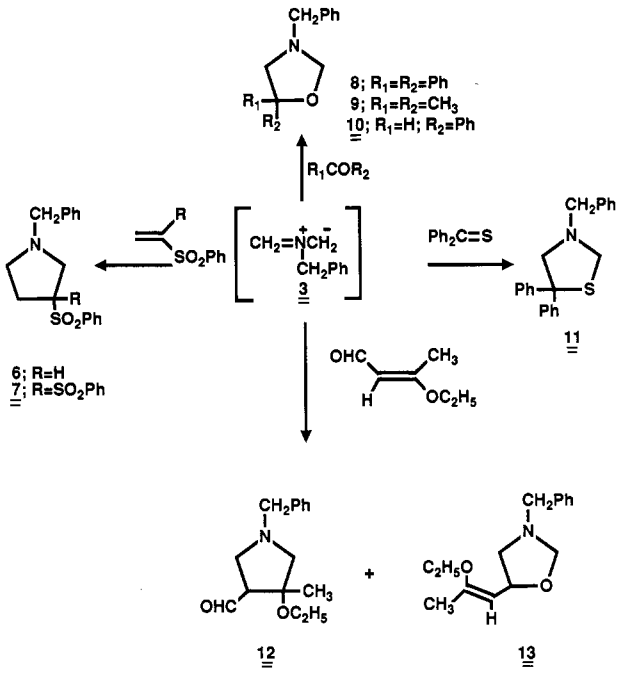
N-[(Trimethylsilyl)methyl]amino ethers have been found to act as azomethine ylide equivalents. Treatment of these compounds with lithium fluoride in the presence of a reactive dipolarophile afforded dipolar cycloadducts in high yield. The cycloaddition proceeded with complete stereospecificity with dimethyl fumarate and maleate. This result is consistent with the intermediacy of an azomethine ylide. The reaction of *N*-benzyl-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine afforded several silylated diamines when treated with zinc chloride or cesium fluoride in the absence of a trapping agent. This can be attributed to an initial loss of the methoxy group to give a transient iminium ion. This species reacts further with the azomethine ylide or undergoes hydrolysis to give a silylated amine. The cycloaddition behavior of several unsymmetrically substituted azomethine ylide precursors was also examined. Competitive rate studies showed that the cycloaddition is compatible with a HOMO-controlled process. The regiochemistry of the cycloaddition, however, is not easily rationalized by simple FMO considerations and may instead be related to the charge transfer interaction energy of the reaction.

The development of versatile methods for forming the five-membered pyrrolidine ring under mild conditions is a central objective of alkaloid synthesis.[1] Several years ago, the dipolar cycloaddition reaction of azomethine ylides attracted our attention as a particularly appealing method for pyrrolidine synthesis.[2-4] Studies conducted in these[5] and other laboratories[6-11] have show that the desilylation of α-trimethylsilyl onium salts represents a convenient method for azomethine ylide generation. More recently, we have described the use of α-(cyanomethyl)aminosilanes as convenient azomethine ylide precursors.[12] Exposure of these compounds to silver fluoride promotes a metal-assisted decyanation to an iminium salt[13,14] and a con-

Scheme I



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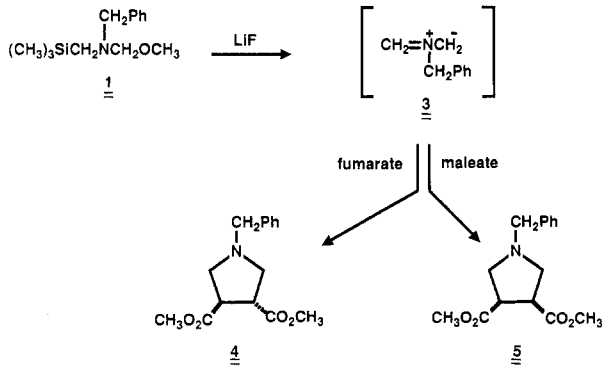
comitant desilylation[15] to give the unsubstituted 1,3-dipole. Although the cycloaddition reaction generally proceeds in good yield (40–80%), it would be particularly useful to be able to generate the dipole without using silver salts. In this paper, we describe our latest results, which use *N*-[(trimethylsilyl)methyl]amino ethers as azomethine ylide precursors.[16]

Results and Discussion

Cycloaddition Studies. *N*-Benzyl-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine (**1**) was prepared in multigram quantities by treating *N*-benzyl-*N*-[(trimethylsilyl)methyl]amine[12] with formaldehyde in the presence of methanol. Cycloaddition of the azomethine ylide derived from **1** with a series of dipolarophiles, as generalized in the conversion of **1** to **2**, was carried out as follows: To a stirred solution of **1** (1 mmol), the appropriate dipolarophile (1 mmol), and 2 mL of acetonitrile was added 1.25 equiv of lithium fluoride. The reaction mixture was sonicated at 35 °C for 5 h and was poured into water. Extractive workup (ether) afforded the 1,3-dipolar cycloadduct in excellent yield (80–95%). The cycloadditions also occurred when zinc chloride or cesium fluoride were used as desilylating agents. Of the various desilylating agents examined, however, lithium fluoride proved to be the most effective. All octet-stabilized 1,3-dipoles examined so far in the literature have been shown to undergo stereospecific cis cycloaddition.[17] In order to determine whether the cycloaddition of methoxymethyl silyl amine **1** proceeds stereospecifically, we studied the reaction with cis and trans disubstituted dipolarophiles. The cycloaddition proceeded with complete stereospecificity with dimethyl fumarate and maleate, giving rise to cycloadducts **4** and **5**. This result is consistent with the intermediacy of azomethine ylide **3**.



A variety of electron-deficient olefins other than carbomethoxy-substituted alkenes is usable, and the results are outlined in Scheme I. The reaction with ethoxymethacrolein produced a mixture of two products (**12** and **13**) (2:1 ratio) corresponding to cycloaddition across the activated π-bond as well as the aldehyde group. Cycloaddition across the carbonyl functionality was also observed to occur with benzaldehyde, benzophenone, and acetone. Thiobenzophenone also proved to be an effective dipolarophile. All attempts to obtain a cycloadduct from the reaction of **1** with nonactivated olefins (i.e., 1-octene, norbornene, etc.) failed. Azomethine ylides generally prefer to react with electron-deficient alkenes and alkynes, since such a pair of addends possesses a narrow dipole HOMO–dipolarophile LUMO gap.[18,19]

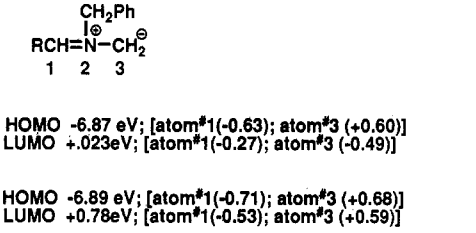


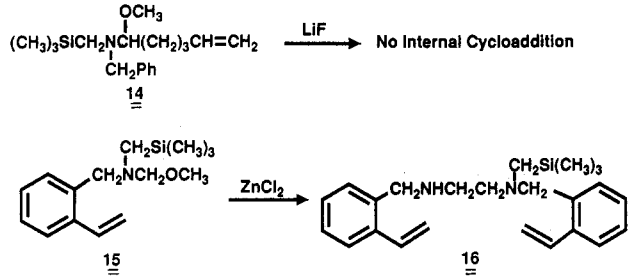
Figure 1. Frontier molecular orbital coefficients and energy levels of substituted azomethine ylides calculated by MNDO.

Table I. Relative Reactivity of Dipolarophiles toward Azomethine Ylide 3 by Direct Competition Methods

dipolarophile	relative rates	LUMO energy
bis(*p*-tolylsulfonyl)ethylene	1.0	*a*
benzaldehyde	1.35	0.81
thiobenzophenone	1.65	0.06
dimethylfumarate	2.58	−0.09
N-phenylmaleimide	3.11	−1.08

[a] LUMO energy not available from MNDO calculations.

Attempted Intramolecular Cycloadditions. As intramolecular cycloadditions exhibit enhanced reactivity and stereoselectivity over their bimolecular counterparts,[21] we reasoned that the reaction of (methoxyhexenyl)amine **14** with lithium fluoride might not suffer the difficulties of cycloaddition to an unactivated π-bond and that an adduct with the desired substitution pattern of the mesembrine family of alkaloids might be obtained. We found, however, that no signs of an internal cycloadduct could be detected in the crude reaction mixture.



Our attention was next given to the possible intramolecular cycloaddition of *o*-vinylbenzyl methoxy amine **15** since this material possesses an aryl activated π-bond.

(15) Colvin, E. W. *Chem. Soc. Rev.* **1978**, *7*, 15. Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.

(16) For related work, see: Hosomi, A.; Sakata, Y.; Sakurai, H. *Chem. Lett.* **1984**, 1117.

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(18) Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 7301.

(19) It should be noted that Roussi and coworkers have recently reported that trimethylene *N*-oxide undergoes reaction with LDA to give an azomethine ylide, which cycloadds with simple alkyl-substituted alkenes.[20] It is not clear to us why azomethine ylides derived from **1** do not undergo 3 + 2 cycloaddition with alkyl-substituted olefins. Further work is needed to establish this point.

(20) Beugelmans, R.; Negron, G.; Roussi, G. *J. Chem. Soc., Chem. Commun.* **1983**, 31. Beugelmanns, R.; Benadijila-Iguertsira, L.; Roussi, G. *J. Chem. Soc., Chem. Commun.* **1982**, 544. Chastanet, J.; Roussi, G. *Heterocycles* **1985**, *23*, 653. Chastanet, J.; Roussi, G. *J. Org. Chem.* **1985**, *50*, 2910. Beugelmanns, R.; Benadijila-Iguertsira, L.; Chastanet, J.; Negron, G.; Roussi, G. *Can. J. Chem.* **1985**, *63*, 725.

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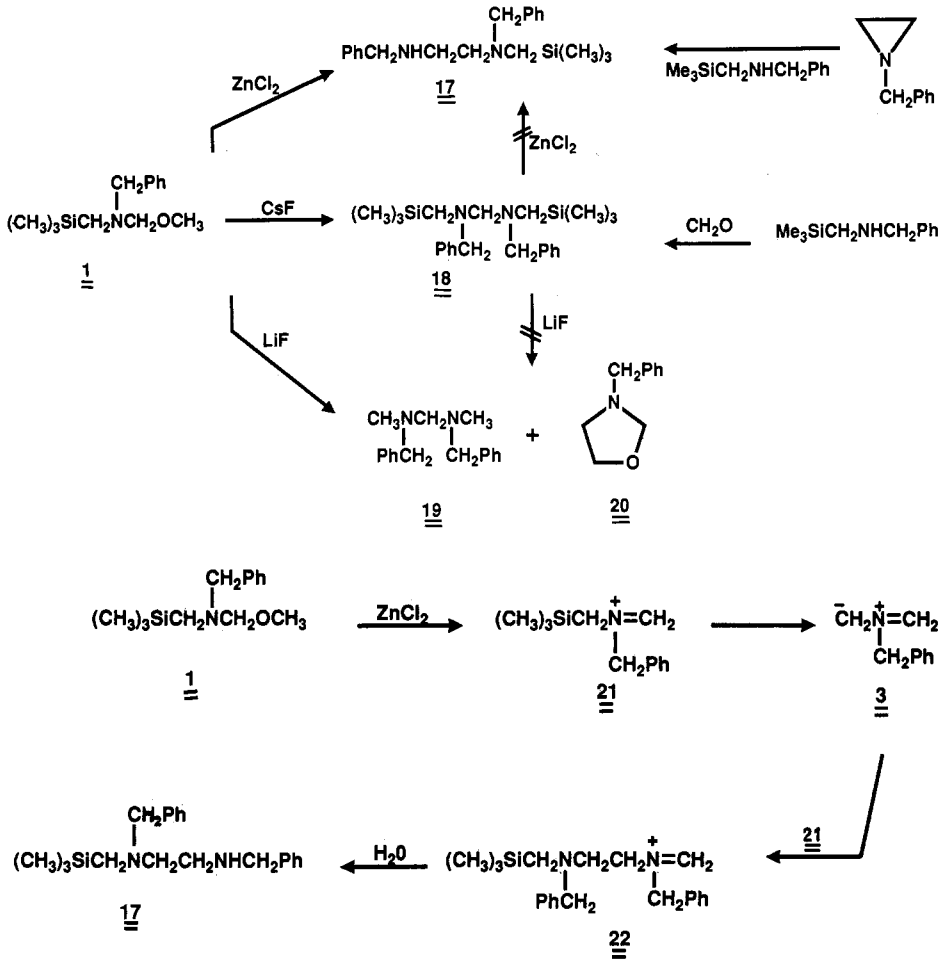
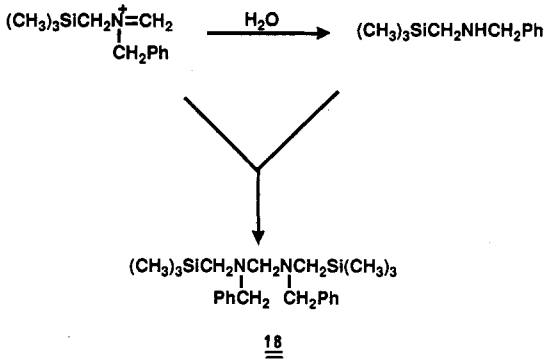


Treating this compound with zinc chloride at 25 °C for 10 h produced the monosilylated diamine **16** in 40% yield as the only characterizable product. No signs of an intramolecular cycloadduct could be detected in the crude reaction mixture. It would seem as though the favorable entropy of reaction is not sufficient to overcome the unfavorable electronic factors.

Desilylation Studies. The above result prompted us to examine the reaction between zinc chloride and methoxy silyl amine **1** in the absence of a trapping agent. We found that the reaction proceeded in an analogous fashion to that encountered with **15** and gave the monosilylated diamine **17** in 80% yield. The identity of **17** was determined by its straightforward spectral properties and by comparison with an independently synthesized sample prepared by treating *N*-benzylaziridine with *N*-benzyl-*N*-[(trimethylsilyl)methyl]amine. It is particularly interesting to note that an entirely different product was obtained when methoxy silyl amine **1** was treated with cesium fluoride. The major product (75%) isolated was identified as the disilylated diamine **18** by comparison with an authentic sample prepared by treating *N*-benzyl-*N*-[(trimethylsilyl)methyl]amine with formaldehyde. A control experiment showed that **18** was not converted to **17** when treated with zinc chloride. The reaction of **1** with lithium fluoride took still another course, producing *N,N'*-dimethyl-*N,N'*-dibenzyldiaminomethane (**19**) and *N*-benzyloxazolidine (**20**). Both of these structures were established by comparison with authentic samples. It should also be pointed out that **18** did not produce **19** upon treatment with LiF.

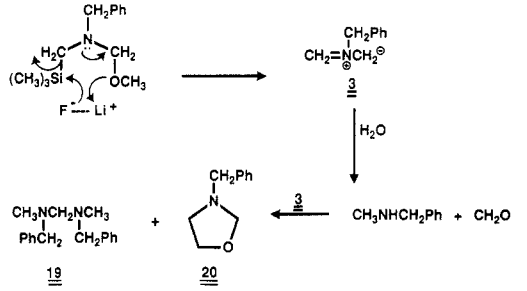
α-Methoxy amines can be considered as latent forms of iminium salts due to their ability to lose methoxide ion on treatment with Lewis acids. Thus, the reaction of **1** with zinc chloride can be most reasonably explained by assuming initial formation of iminium ion **21** followed by a subsequent desilylation to generate azomethine ylide **3**. In the absence of a trapping agent, the 1,3-dipole reacts with **21** to give a new iminium ion **22**, which eventually affords the observed product **17** on hydrolytic workup.

In order to rationalize the difference in product distribution when cesium fluoride was used as the desilylating agent, we propose that the initially formed iminium ion **21** undergoes a prior hydrolysis to the [(trimethylsilyl)methyl]amine and formaldehyde. Apparently, the batch of cesium fluoride that was used contained a significant amount of water, which resulted in hydrolysis rather than desilylation to the ylide. Once the [(trimethylsilyl)methyl]amine was formed, it reacted with **21** to give the disilylated diamine **18**.

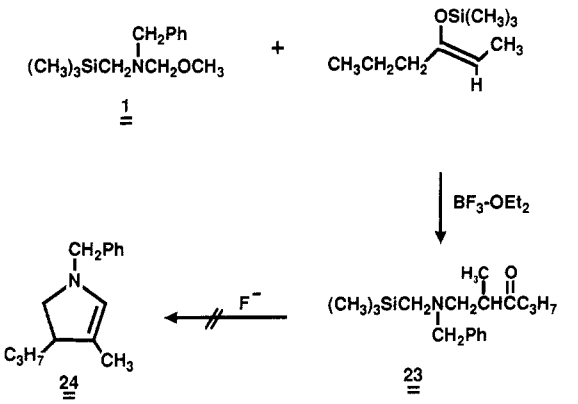


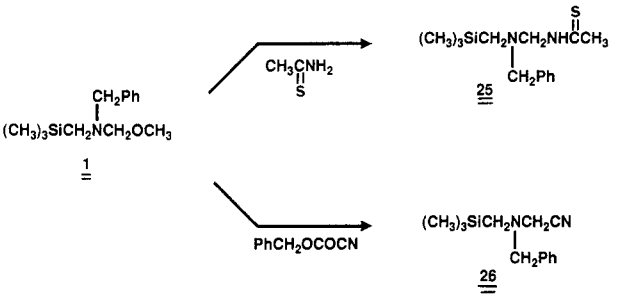
In contrast to cesium fluoride, the reaction of **1** with LiF afforded no signs of a disilylated product. Although onium salt desilylation using a variety of nucleophiles has been

described,[22,23] it is generally thought that fluoride ion is the best "silylophile" for ylide generation.[6] All naked fluoride sources tend to be highly hydroscopic, but LiF has the advantage that it is relatively anhydrous and less soluble in acetonitrile than cesium fluoride. This would tend to minimize the amount of water present in solution and thereby suppress the hydrolysis reaction. More than likely, formation of the azomethine ylide proceeds in a concerted fashion when LiF is used. The "hard" lithium promotes loss of the methoxy group at the same time that fluoride ion attacks silicon. In the absence of a trapping agent, the resulting dipole will eventually react with small amounts of water still present in solution to generate benzylmethylamine and formaldehyde. Both of these compounds, in turn, react further to give the observed products (i.e., **19** and **20**).



Half-Capped Dipoles. Simple and stable reagents possessing a nucleophilic and an electrophilic site, which can be deployed selectively and sequentially, are of great potential use in synthesis. On the basis of the results encountered with methoxy silyl amine **1** and zinc chloride, it occurred to us that compound **1** might be "decapped" in a sequential fashion, thereby broadening the use of this material in organic synthesis. In light of our previous findings, and in view of the elegant investigations of Danishefsky et al.[24] and Mukaiyama et al.,[25] we examined the reaction of a representative silyl enol ether with methoxy silyl amine **1** under the influence of boron trifluoride etherate. This reaction led to formation of ketone **23** in 70% yield. The formation of **23** undoubtedly proceeds via a silyliminium ion, which reacts with the silyl enol ether. It is evident from this result that methoxy silyl amine **1** can be used in a sequential fashion to generate a "half-capped" dipole. Unfortunately, numerous attempts to cyclodesilylate structure **23** (i.e., **23**→**24**) failed, and

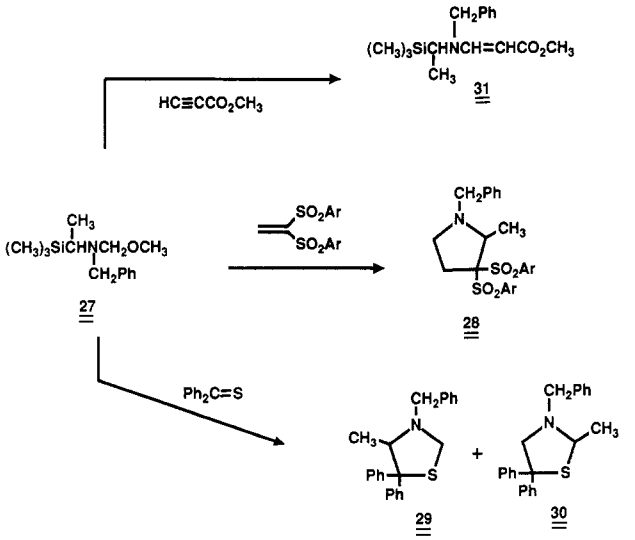




further work with this system was abandoned. We also studied the Lewis acid catalyzed reaction of methoxy silyl amine **1** with thioacetamide and benzyl cyanoformate. As was found in the corresponding reaction of **1** with silyl enol ethers, the sole products were those arising from displacement of the methoxy group. The generalization of these findings and their implications for the synthesis of various alkaloids are the object of ongoing investigations.

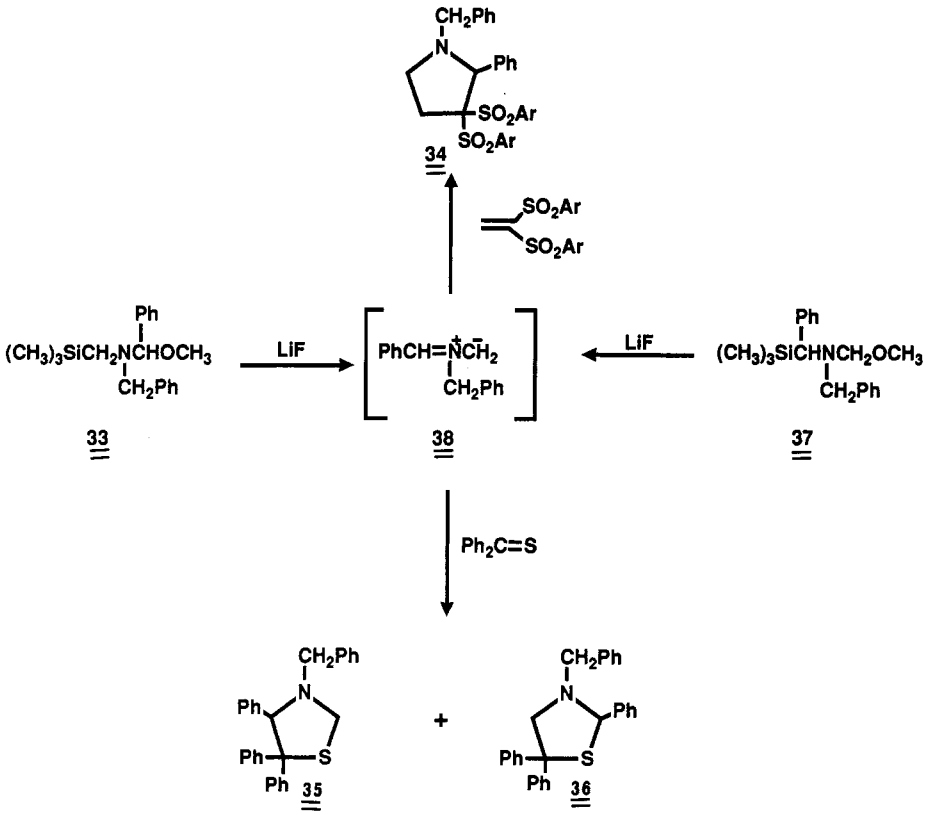
Mechanistic Considerations. The observations presented above clearly demonstrate that pyrrolidines can be readily synthesized from methoxy silyl substituted amines. Formation of a nonstabilized azomethine ylide by attack on a silicon substituted onium salt intermediate is a well-known reaction.[6-12] In any nucleophilic desilylation process, however, the question arises as to whether or not a silicon-free intermediate is responsible for the apparent ylide reactions. Although a pentavalent silicon species can precede ylide formation, it is conceivable that the dipolarophile might react with a "half-capped" dipole in a stepwise fashion to give cycloadducts without the actual involvement of an azomethine ylide.

Information about the mechanistic details of the reaction has come from a study of the regiochemistry of cycloaddition of several unsymmetrically substituted systems. As our first model, we chose to investigate the reaction of *N*-benzyl-*N*-[α-(trimethylsilyl)ethyl]-*N*-(methoxymethyl)amine (**27**) with several different types of dipolarophiles. Treatment of **27** with LiF in the presence of



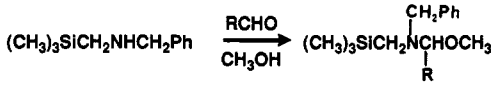
1,1-bis(*p*-tolylsulfonyl)ethylene produced a single cycloadduct, whose structure was assigned as **28** on the basis of its spectral data (see Experimental Section). In contrast to this result, the reaction of **27** with thiobenzophenone resulted in a 3:2 mixture of cycloadducts **29** and **30**. We also studied the reaction of **27** with methyl propiolate. Numerous attempts to isolate a cycloadduct from this reaction failed. The only material that we could isolate corresponded to the conjugate addition of *N*-benzyl-α-

(22) Sato, Y.; Ban, Y.; Aoyama, T.; Shirai, H. *J. Org. Chem.* **1976**, *41*, 1962. Sato, Y.; Ban, Y.; Aoyama, T.; Shirai, H. *J. Org. Chem.* **1976**, *41*, 3559.
(23) Sekiguchi, A.; Ando, W. *J. Org. Chem.* **1979**, *44*, 413.
(24) Danishefsky, S.; Guingant, A.; Prisbylla, M. *Tetrahedron Lett.* **1980**, *21*, 2033.
(25) Mikaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503. Narasaka, K.; Soai, K.; Mukaiyama, T. *Chem. Lett.* **1974**, 1223.



methyl-α-(trimethylsilyl)methylamine across the activated triple bond.

Formation of the identical ratio of cycloadducts from the isomeric silyl methoxy amine **32** would provide convincing support for the involvement of an azomethine ylide intermediate. Unfortunately, our efforts to synthesize



32; R=CH_3
33; R=Ph

compound **32** by treating *N*-benzyl-*N*-[(trimethylsilyl)-methyl]amine with acetaldehyde in the presence of methanol failed to give the desired compound. This was due to a competitive aldol condensation. Instead, we prepared the closely related phenyl-substituted silyl methoxy amine **33**. Treatment of this material with 1,1-bis(*p*-tolylsulfonyl)ethylene afforded a single cycloadduct identified as **34** on the basis of its spectral properties. A mixture of two cycloadducts **35** and **36** (3:2) was formed by stirring **33** with thiobenzophenone in the presence of lithium fluoride. Most importantly, the reactions of the isomeric silyl methoxy amine **37** with thiobenzophenone and the disulfonylethylene afforded the same distribution of cycloadducts as that obtained from **33**. This result strongly implicates azomethine ylide **38** as a common intermediate in these reactions.

Regiochemistry and FMO Theory. The perturbational approach is a powerful tool for investigating various aspects of 1,3-dipolar cycloaddition chemistry.[18] Even in its crudest approximation, namely the frontier orbital approximation, success has often been achieved in spite of considerable doubt as to its theoretical foundation.[26] When azomethine ylides are used as 1,3-dipoles, the dipole highest occupied (HOMO) and dipolarophile lowest unoccupied (LUMO) orbital interaction stabilizes the transition state. Competitive studies of a series of dipolarophiles with methoxy silyl amine **1** (see Table I) show that the rate of the cycloaddition is proportional to the LUMO energy of the dipolarophile. This is in accordance with the known influence of substituents on the LUMO energy of ethylene,[27] only electron-attracting groups increase the dipolarophilic activity.[28] The orientation of cycloaddition of an unsymmetrical azomethine ylide is related to the HOMO coefficient in the dipole, which is the nucleophilic partner in this reaction. The stabilization of the two regioisomeric transition states arising from this HOMO–LUMO interaction depends upon interaction terms $C_aC_b\gamma_{ab}S_{ab}$, where C_a and C_b are coefficients of frontier orbitals at centers a and b, S_{ab} is the overlap integral for atomic orbitals at the centers, and γ_{ab} is the proportionality between overlap and stabilization for a given atom pair. Since the details of transition-state geometry are not known, we cannot evaluate γ_{ab}. MNDO calculations of methyl and phenyl azomethine ylides **39** and **38**, respectively, indicate that the largest coefficient in the HOMO resides on the substituted carbon atom of the dipole. The lack of regiospecificity exhibited by thiobenzophenone with the unsymmetrically substituted azomethine ylides **38** and **39** is not unreasonable since the MNDO calculations indicate little difference in the size of the coefficients in the LUMO orbital. It is clear from the literature[18] and our own MO calculations that the largest coefficient in 1,1-bis(*p*-tolylsulfonyl)ethylene resides on the β-carbon atom. This should become linked with the more substituted carbon atom of the azomethine ylide (i.e., atom no. 1), which represents the site of the largest HOMO coefficient. However, this prediction of regiose-

(26) Stone, A. J. In *Theoretical Chemistry*; Dixson, R. N., Tomson, C., Eds.; Chemical Society: London, 1976; Vol. 3, p 39.

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lectivity is not in agreement with the experimental results. Thus, the regiochemistry of the cycloaddition of ylides **38** and **39** with the disulfonyl-substituted ethylene must be related to other factors. Steric hindrance does not appear to play a role here since the more congested cycloadduct is formed (i.e., **34** and **28**). The insufficient agreement with experiment may be due to inadequacies in the MNDO calculations, mostly involving the orbital coefficients in the HOMO of the dipole. However, it should be stressed that the Klopman–Salem equation[29] relates to an early point on the reaction path, so that it can account for only a fraction of the activation energy. An alternate possibility is that the regiochemistry is related to the charge transfer interaction energy of the cycloaddition. In the present case, the disulfonyl-substituted ethylene may induce an inhomogeneous electric field in the vicinity of the approaching dipole and van der Waals energy considerations may become important in determining regioselectivity. Further work with a variety of unsymmetrically substituted dipolarophiles is currently in progress in order to establish this point. We are continuing to examine silyl methoxy substituted amines as azomethine ylide precursors and will report additional findings at a later date.

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 a Varian EM-390 and Nicolet FT-360 spectrometer. ^{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 Finnegan 4000 mass spectrometer at an ionizing voltage of 70 eV.

Preparation of *N*-Benzyl-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine (1). To a stirred 37% aqueous formaldehyde solution (6.0 g) at 0 °C was slowly added 10 g of *N*-benzyl-*N*-[(trimethylsilyl)methyl]amine.[12] After the mixture was stirred for 10 min, 6 mL of methanol was added and the resulting solution was saturated with potassium carbonate. The mixture was stirred for 1 h, and the nonaqueous phase was separated and stirred overnight with an excess of potassium carbonate. The solvent and excess alcohol were removed under reduced pressure, and the product was isolated by distillation in 72% yield: bp 78–80 °C (0.5 mm); NMR (90 MHz, $CDCl_3$) δ 0.10 (s, 9 H), 2.13 (s, 2 H), 3.20 (s, 3 H), 3.72 (s, 2 H), 3.95 (s, 2 H), and 7.22 (m, 5 H); IR (neat) 3095, 3030, 1605, 1495, 1422, 1362, 1245, 925, 740, 700 cm^{-1}. Anal. Calcd for $C_{13}H_{23}NOSi$: C, 65.77; H, 9.76; N, 5.90. Found: C, 65.77; H, 9.77; N, 5.87.

General Procedure for Cycloaddition of 1 with Various Dipolarophiles. A solution containing 1 mmol of *N*-benzyl-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine, 1 mmol of the dipolarophile, and 1.25 mmol of the desilylating reagent in 0.5 M acetonitrile was sonicated at 35 °C for 5 h. The reaction was poured into water and extracted with ether. The ethereal extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The reactions were chromatographed on silica gel with an ethyl acetate–hexane mixture as the eluent to give the following cycloadducts: benzaldehyde (*N*-benzyl-5-phenyloxazolidine, 80%), fumaronitrile (*N*-benzyl-*trans*-3,4-dicyanopyrrolidine, 85%), dimethyl fumarate (*N*-benzyl-*trans*-3,4-dicarbomethoxypyrrolidine, 90%), dimethyl maleate (*N*-benzyl-*cis*-3,4-dicarbomethoxypyrrolidine, 90%), *N*-phenylmaleimide (2,6-dioxo-1-phenyl-4-benzyl-1,4-diazobicyclo[3.3.0]octane, 98%).[12]

Cycloaddition of 1 with Phenyl Vinyl Sulfone in the Presence of Cesium Fluoride. To a solution containing 240 mg of 1 and 170 mg of phenyl vinyl sulfone in 4 mL of acetonitrile was added 160 mg of cesium fluoride, and the resulting solution was sonicated for 5 h. The reaction mixture was poured into water and extracted with ether. The ether extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography with a 30% ethyl acetate–hexane mixture as the eluent. The major fraction contained 0.27 g (92%) of a clear oil, whose structure was assigned as *N*-benzyl-3-(phenylsulfonyl)-pyrrolidine (**6**) on the basis of its spectral properties: IR (neat) 3020, 2800, 1610, 1590, 1500, 1450, 1320, 1150, 1030, 930, 740, and 700 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.0–2.2 (m, 1 H), 2.24–2.35 (m, 1 H), 2.41–2.61 (m, 1 H), 2.65–2.75 (m, 1 H), 2.87 (d, 1 H, J = 11.0 Hz), 3.57 (d, 1 H, J = 12.0 Hz), 3.64 (d, 1 H, J = 12.0 Hz), 3.67–3.78 (m, 1 H), and 7.3–7.9 (m, 10 H); C^{13} NMR ($CDCl_3$, 50 MHz) δ 25.9, 53.2, 53.7, 59.5, 62.8, 127.1, 128.2, 128.5, 129.1, 133.5, 138.3, and 138.7. Anal. Calcd for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.37; N, 4.65. Found: C, 67.62; H, 6.40; N, 4.58.

The second fraction isolated from the column contained 30 mg (8%) of *N*-benzyl-*N*-[(trimethylsilyl)methyl]-*N*-[β-(phenylsulfonyl)ethyl]amine, which was identified on the basis of its spectral properties: IR (neat) 3040, 2950, 1500, 1450, 1300, 1150, 850, and 700 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.10 (s, 9 H), 1.98 (s, 2 H), 2.7–3.0 (m, 1 H), 3.0–3.3 (m, 1 H), 3.47 (s, 2 H), 7.15 (s, 5 H), and 7.3–8.0 (m, 5 H). Anal. Calcd for $C_{19}H_{27}NO_2SSi$: C, 63.10; H, 7.54; N, 3.87. Found: C, 63.19; H, 7.56; N, 3.87.

The structure of this material was verified by an independent synthesis. A solution containing 500 mg of *N*-benzyl-*N*-[(trimethylsilyl)methyl]amine,[12] 440 mg of phenyl vinyl sulfone, and 200 mg of zinc chloride in 6 mL of acetonitrile was sonicated for 5 h. The reaction mixture was poured into water and extracted with ether. The ethereal extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified on a silica gel column with a 35% ethyl acetate–hexane mixture as the eluent. The major fraction contained 600 mg (65%) of a clear oil, whose structure was assigned as *N*-benzyl-*N*-[(trimethylsilyl)methyl]-*N*-[(β-phenylsulfonyl)-ethyl]amine. This material was identical with the minor fraction obtained from the reaction of *N*-benzyl-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine with phenyl vinyl sulfone in the presence of cesium fluoride.

Cycloaddition of 1 with 1,1-Bis(*p*-tolylsulfonyl)ethylene in the Presence of Lithium Fluoride. A solution containing 180 mg of 1, 250 mg of 1,1-bis(*p*-tolylsulfonyl)ethylene,[30] and 30 mg of lithium fluoride in 3 mL of acetonitrile was sonicated for 5 h. The reaction mixture was poured into water and extracted with ether. The combined ether extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography with a 30% ethyl acetate–hexane mixture as the eluent. The major fraction isolated contained 0.16 g (45%) of a white solid (mp 149–150 °C), whose structure was assigned as *N*-benzyl-3,3-bis-(*p*-tolylsulfonyl)pyrrolidine (**7**) on the basis of its spectral properties: IR (KBr) 1600, 1460, 1300, 1170, 1080, 820, and 770 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.45 (s, 6 H), 2.6–2.75 (m, 4 H), 3.24 (s, 2 H), 3.56 (s, 2 H), 7.2–7.4 (m, 9 H), and 7.8–7.9 (m, 4 H); MS, m/e 469 (M^+), 167, 149, and 91; UV (95% ethanol) 253 nm (ϵ 26 800). Anal. Calcd for $C_{25}H_{27}NO_4S_2$: C, 63.94; H, 5.80; N, 2.98. Found: C, 63.61; H, 5.83; N, 2.96.

Cycloaddition of 1 with Benzophenone in the Presence of Lithium Fluoride. A solution containing 300 mg of 1, 230 mg of benzophenone, and 40 mg of lithium fluoride in 4 mL of acetonitrile was sonicated for 5 h. The reaction mixture was poured into water and extracted with methylene chloride. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting residue was subjected to flash silica gel chromatography with a 20% ethyl acetate–hexane mixture as the eluent. The major product isolated contained 0.16 g (40%) of a clear oil, whose structure was assigned as *N*-benzyl-5,5-diphenyloxazolidine (**8**) on the basis of its spectral properties: IR (neat) 3040, 2920, 1500, 1370, 1150, 1020, 950, 750, and 700 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 3.60 (s, 2 H), 3.64 (s, 2 H), 4.62 (s, 2 H), and 7.1–7.4 (m, 15 H); MS, m/e 315 (M^+), 200, 133, 91, and 77. Anal. Calcd for $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.52; H, 6.83; N, 4.22.

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Cycloaddition of 1 with Acetone in the Presence of Lithium Fluoride. A solution containing 300 mg of 1 and 40 mg of lithium fluoride in 3 mL of anhydrous acetone was sonicated for 5 h. The reaction mixture was poured into water and extracted with ether. The combined ether extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residue obtained was subjected to flash silica gel chromatography with a 15% ethyl acetate–hexane mixture as the eluent. The major fraction contained 150 mg (60%) of a clear oil, whose structure was assigned as *N*-benzyl-5,5-dimethyloxazolidine (**9**) on the basis of its spectral properties: IR (neat) 2980, 1500, 1460, 1250, 1070, 750, and 700 cm^{-1}; NMR (CCl_4, 90 MHz) δ 1.26 (s, 6 H), 2.57 (s, 2 H), 3.67 (s, 2 H), 4.18 (s, 2 H), and 7.0–7.3 (m, 5 H); MS, *m/e* 191 (M^+), 133, 101, and 91. Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.11; H, 9.00; N, 7.26.

Cycloaddition of 1 with Thiobenzophenone. A solution containing 0.21 g of thiobenzophenone, 0.25 g of 1, and 0.03 g of lithium fluoride in 3 mL of dry acetonitrile was subjected to sonication for 12 h. The reaction mixture was filtered, and the solvent was removed under reduced pressure to give a light yellow oil. The crude material was subjected to silica gel chromatography with a 10% ethyl acetate–hexane mixture as the eluent. The major product isolated contained 0.31 g (91%) of a thick oil, whose structure was assigned as *N*-benzyl-5,5-diphenylthiazolidine (**11**) on the basis of its spectral data: NMR (90 MHz, $CDCl_3$) δ 3.59 (s, 2 H), 3.63 (s, 2 H), 4.12 (s, 2 H), and 7.1–7.8 (m, 15 H); IR (neat) 3060, 2925, 2800, 1600, 1495, 1318, 760, and 700 cm^{-1}. Anal. Calcd for $C_{22}H_{21}NS$: C, 79.72; H, 6.39; N, 4.22; S, 9.67. Found: C, 79.67; H, 6.38; N, 4.20; S, 9.60.

Cycloaddition of 1 with Ethoxymethacrolein. A solution containing 0.10 g of ethoxymethacrolein, 0.25 g of 1, and 0.03 g of lithium fluoride in 3 mL of dry acetonitrile was sonicated for 12 h. The solution was filtered, and the solvent was removed under reduced pressure. The crude residue was subjected to silica gel chromatography with a 20% ethyl acetate–hexane mixture as the eluent. The first fraction isolated from the column contained 81 mg (41%) of a colorless oil, whose structure was assigned as 1-benzyl-3-ethoxy-3-methylpyrrolidine-4-carboxaldehyde (**12**) on the basis of its spectral data: NMR (90 MHz, $CDCl_3$) δ 1.12 (s, 3 H), 1.15 (t, 3 H, J = 6.0 Hz), 2.26 (m, 2 H), 3.10 (m, 2 H), 3.43 (q, 2 H, J = 6.0 Hz), 3.61 (s, 2 H), 4.12 (t, 1 H, J = 6.0 Hz), 7.32 (m, 5 H), 9.63 (s, 1 H); IR (neat) 3040, 2985, 1725, 1605, 1460, 1360, 1110, 910, 800, and 700 cm^{-1}. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 73.16; H, 8.24; N, 5.97.

The second fraction isolated from the column contained 50 mg (21%) of a colorless oil, whose structure was assigned as 3-benzyl-5-(2-ethoxyprop-1-enyl)oxazolidine (**13**) on the basis of the following spectral data: NMR (90 MHz, $CDCl_3$) δ 1.25 (t, 3 H, J = 6.0 Hz), 1.63 (s, 3 H), 2.88 (m, 2 H), 3.80 (s, 2 H), 3.80 (q, 2 H, J = 6.0 Hz), 4.36 (m, 1 H), 4.42 (s, 2 H), 6.15 (s, 1 H), 7.38 (m, 5 H); IR (neat) 3075, 1684, 1610, 1500, 1390, 1310, 1135, 1075, 920, and 704 cm^{-1}.

Preparation and Attempted Cycloaddition of *N*-Benzyl-*N*-[(trimethylsilyl)methyl]-*N*-(1-methoxyhex-5-enyl)amine (14). To a 0.59-g sample of 5-hexenal cooled to 0 °C was slowly added 1.0 g of *N*-benzyl-*N*-[(trimethylsilyl)methyl]amine[12] over a 30-min time span. To this mixture was added 1.5 mL of methanol, and the solution was saturated with potassium carbonate. After the mixture was stirred for 8 h, the organic layer was separated and the excess solvent was removed under reduced pressure. The crude residue was purified by molecular distillation to give 1.02 g (53%) of a colorless oil, whose structure was assigned as *N*-benzyl-*N*-[(trimethylsilyl)methyl]-*N*-1-methoxyhex-5-enylamine (**14**) on the basis of its characteristic spectral data: bp 140 °C (0.02 mm); NMR (90 MHz, $CDCl_3$) δ 0.10 (s, 9 H), 1.4–2.4 (m, 8 H), 3.20 (s, 3 H), 3.70 (s, 2 H), 3.9 (m, 1 H), 4.9–5.2 (m, 2 H), 5.7–6.1 (m, 1 H), and 7.3 (s, 5 H); IR (neat) 3040, 1645, 1500, 1460, 1130, 1000, 875, and 705 cm^{-1}. Anal. Calcd for $C_{18}H_{31}NOSi$: C, 70.76; H, 10.23; N, 4.58. Found: C, 70.70; H, 10.41; N, 4.54.

A solution containing 0.5 g of **14** and 0.1 g of lithium fluoride in 5 mL of dry acetonitrile was sonicated for 20 h. The only material that was obtained from the chromatographic separation was recovered starting material. The reaction was repeated except that the above solution was sealed in a thermolysis tube under an argon atmosphere and was heated in an oil bath at 130 °C for 24 h. No sign of any cycloaddition products could be detected in the crude reaction mixture.

Preparation of *N*-(*o*-Vinylbenzyl)-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine (15). A solution containing 2.0 g of *o*-vinyl benzyl chloride[31] and 2.7 g of [(trimethylsilyl)methyl]amine[32] in 60 mL of benzene was heated at reflux for 36 h. At the end of this time, a 5% sodium hydroxide solution was added to the mixture in order to hydrolyze the white organic salt that had formed. The mixture was extracted with ether, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a brown oil. The resulting residue was purified on the chromatotron unit with a 10% ethyl acetate–hexane mixture as the eluent. The major fraction contained 2.25 g (78%) of *N*-(*o*-vinylbenzyl)-*N*-[(trimethylsilyl)methyl]amine as a yellow oil: IR (neat) 3020, 1630, 1490, 1360, 1250, 1020, 910, 840, and 760 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.10 (s, 9 H), 3.78 (s, 2 H), 5.21 (dd, 1 H, J = 12.0 and 2.5 Hz), 5.60 (dd, 1 H, J = 15.0 and 12.5 Hz), 7.02 (dd, 1 H, J = 15.0 and 12.0 Hz), and 7.1–7.5 (m, 4 H).

A sample containing 0.5 g of the above compound was added dropwise to 0.24 g of a 37% aqueous formaldehyde solution at 0 °C. Methanol was introduced in one portion, and the solution was saturated with potassium carbonate. After the mixture was stirred for 1 h, the organic layer was separated and saturated again with fresh potassium carbonate. The mixture was stirred overnight, diluted with anhydrous ether, filtered, and concentrated under reduced pressure to give 0.52 g (85%) of a clear oil. This material was assigned as *N*-(*o*-vinylbenzyl)-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine (**15**) on the basis of its spectral properties: IR (neat) 3020, 1630, 1490, 1390, 1250, 1070, 920, 770, and 700 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.10 (s. 9 H), 2.20 (s, 2 H), 3.18 (s, 3 H), 3.79 (s, 2 H), 3.93 (s, 2 H), 5.21 (dd, 1 H, J = 12.0 and 2.5 Hz), 5.61 (dd, 1 H, J = 15.0 and 2.5 Hz), 7.12 (dd, 1 H, J = 15.0 and 12.0 Hz), and 7.2–7.6 (m, 4 H).

Reaction of *N*-(*o*-Vinylbenzyl)-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine (15) with Zinc Chloride. A solution containing 600 mg of **15** and 320 mg of zinc chloride in 6 mL of acetonitrile was stirred for 10 h at room temperature. The mixture was taken up in ether, filtered, and concentrated under reduced pressure. The resulting residue was purified on the chromatotron unit with a 5% ethyl acetate–hexane mixture as the eluent. The major fraction contained 120 mg (40%) of a clear oil, whose structure was assigned as *N'*-(*o*-vinylbenzyl)-*N*-(*o*-vinylbenzyl)-*N*-[(trimethylsilyl)methyl]ethylenediamine (**16**) on the basis of its spectral properties: IR (neat) 3080, 1630, 1420, 1250, 910, 770, and 700 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 0.10 (s, 9 H), 1.63 (br s, 1 H), 1.92 (s, 2 H), 2.46 (t, 2 H, J = 6.0 Hz), 2.64 (t, 2 H, J = 6.0 Hz), 3.52 (s, 2 H), 3.67 (s, 2 H), 5.18 (dd, 1 H, J = 10.8 and 1.0 Hz), 5.24 (dd, 1 H, J = 10.8 and 1.1 Hz), 5.52 (dd, 1 H, J = 17.3 and 1.4 Hz), 5.61 (dd, 1 H, J = 17.3 and 1.4 Hz), 6.95 (dd, 1 H, J = 14.0 and 11.2 Hz), 7.15 (dd, 1 H, J = 14.0 and 11.2 Hz), and 7.1–7.3 (m, 8 H).

Reaction of *N*-Benzyl-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine (1) with Zinc Chloride. A solution containing 500 mg of 1 and 300 mg of zinc chloride in 4 mL of acetonitrile was stirred for 10 h at room temperature. The reaction mixture was poured into water and extracted with ether. The ethereal extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a clear oil. This material was subjected to flash chromatography with a 20% ethyl acetate–hexane mixture as the eluent. The major fraction contained 200 mg (80%) of a clear oil, whose structure was assigned as *N,N'*-dibenzyl-*N*-[(trimethylsilyl)methyl]-ethylenediamine (**17**) on the basis of its spectral properties: IR (neat) 3080, 1500, 1360, 1100, 850, and 700 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 0.10 (s, 9 H), 1.90 (s, 2 H), 2.43 (t, 2 H, J = 6.0 Hz), 2.61 (t, 2 H, J = 6.0 Hz), 3.42 (s, 2 H), 3.63 (s, 2 H), and 7.1–7.3 (m, 10 H); MS, *m/e* 326 (M^+), 134, 91, and 74. Anal. Calcd for $C_{20}H_{30}N_2Si$: C, 73.56; H, 9.26; N, 8.58. Found: C, 73.40; H, 9.28; N, 8.51.

The structure of **17** was verified by an independent synthesis. *N*-Benzylaziridine was prepared via the general method of Eld-

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erfield and Hageman.[33] A sample containing 14.5 g of *N*-benzyl-*N*-[(trimethylsilyl)methyl]amine[12] was added dropwise to a mixture containing 7.6 g of anhydrous aluminum chloride in 10 mL of dry benzene at 0 °C. To this solution was added 5.0 g of *N*-benzylaziridine,[33] and the reaction mixture was heated at reflux for 1 h. The mixture was then transferred to a 1-L three-necked flask equipped with a reflux condenser and a mechanical stirrer. The flask was immersed in an ice bath, and 50 g of ice water was added. To the resulting solid mass was added 25.0 g of potassium hydroxide in small portions. After the mixture was stirred for 30 min, the benzene layer was separated. The aqueous layer was extracted with benzene, and the combined organic layers were dried over potassium hydroxide. The solvent was concentrated under reduced pressure, and the resulting yellow oil was subjected to flash chromatography with a 20% ethyl acetate–hexane mixture as the eluent. The major fraction contained 1.8 g (30%) of a clear oil, whose structure was assigned as *N,N'*-dibenzyl-*N*-[(trimethylsilyl)methyl]ethylenediamine (**17**). This material was identical with that obtained from the reaction of *N*-benzyl-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine withzinc chloride.

Reaction of *N*-Benzyl-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine (1) with Cesium Fluoride. A solution containing 500 mg of 1 and 330 mg of cesium fluoride in 5 mL of acetonitrile was sonicated for 5 h. The reaction mixture was poured into water and extracted with methylene chloride. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was distilled at 94 °C under reduced pressure (0.07 mm) to give a clear oil, whose structure was assigned as *N,N'*-dibenzyl-*N,N'*-bis[(trimethylsilyl)methyl]diaminomethane (**18**) on the basis of its spectral properties: IR (neat) 3050, 1605, 1510, 1440, 1410, 1270, 1130, 1050, 940, 880, 760, and 720 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.10 (s, 18 H), 1.98 (s, 4 H), 2.87 (s, 2 H), 3.61 (s, 4 H), and 7.22 (s, 10 H); MS, *m/e* 398 (M^+) 207, 206, 192, and 134. Anal. Calcd for $C_{23}H_{38}N_2Si_2$: C, 69.28; H, 9.61; N, 7.03. Found: C, 69.06; H, 9.64; N, 7.02.

The structure of **18** was further verified by an independent synthesis. A sample containing 1.0 g of *N*-benzyl-*N*-[(trimethylsilyl)methyl]amine[12] was added dropwise to 0.24 g of a 37% aqueous formaldehyde solution at 0 °C. The solution was saturated with potassium carbonate and stirred for 1 h. The organic layer was separated, saturated again with potassium carbonate, and stirred overnight. The reaction mixture was diluted with ether, filtered, and concentrated under reduced pressure. The residue was distilled under reduced pressure (0.07 mm), and the fraction corresponding to *N,N'*-dibenzyl-*N,N'*-bis[(trimethylsilyl)methyl]diaminomethane (**18**), which boiled at 93–94 °C, was collected (0.5 g (60%)). This material was identical in every detail with a sample obtained from the reaction of 1 with cesium fluoride.

Reaction of *N*-Benzyl-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine (1) with Lithium Fluoride. A solution containing 500 mg of 1 and 60 mg of lithium fluoride in 5 mL of acetonitrile was sonicated for 5 h. The reaction mixture was poured into water and extracted with methylene chloride. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a yellow oil. This material was chromatographed on a silica gel column with a 25% ethyl acetate–hexane solution as the eluent. The first fraction contained 0.16 g (43%) of a clear oil, whose structure was assigned as *N,N'*-dibenzyl-*N,N'*-dimethyldiaminomethane (**19**) on the basis of its spectral properties: IR (neat) 3050, 1660, 1620, 1510, 1400, 1280, 1180, 1060, 1000, 760, and 720 cm^{-1}; NMR (CCl_4, 90 MHz) δ 2.18 (s, 6 H), 2.96 (s, 2 H), 3.58 (s, 4 H), and 7.21 (s, 5 H); MS, *m/e* 254 (M^+) 224, 134, and 91. Anal. Calcd for $C_{17}H_{22}N_2$: C, 80.27; H, 8.72; N, 11.01. Found: C, 80.23; H, 8.73; N, 10.97.

The second fraction contained 0.18 g (50%) of a clear oil, whose structure was assigned as *N*-benzyloxazolidine (**20**) on the basis of its spectral properties: IR (neat) 3020, 1610, 1500, 1460, 1160, 1010, 750, and 710 cm^{-1}; NMR (CCl_4, 90 MHz) δ 2.90 (t, 2 H, *J* = 7.0 Hz), 3.68 (s, 2 H), 3.72 (t, 2 H, *J* = 7.0 Hz), 4.20 (s, 2 H), and 7.2–7.4 (m, 5 H). Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.42; H, 8.06; N, 8.53.

The structure of bis(alkylamino)methane **19** was verified by an independent synthesis. A solution containing 0.34 g of a 37% aqueous formaldehyde solution was added dropwise to 1.0 g of *N*-benzylmethylamine in 4.13 mL of a 1.0 N hydrochloric acid solution at 0 °C. The reaction mixture was stirred overnight and poured into a saturated sodium bicarbonate solution. The solution was extracted with ether, washed with a saturated sodium bicarbonate solution, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was distilled under vacuum at 65 °C (0.06 mm) to give 0.4 g (60%) of a clear oil, whose structure was identical with that of a sample of **19** obtained from the reaction of 1 with lithium fluoride.

The structure of *N*-benzyloxazolidine (**20**) was also further verified by an independent synthesis. A sample containing 2.0 g of *N*-benzylethanolamine was added dropwise to 1.15 g of a 37% aqueous formaldehyde solution at 0 °C. The solution was saturated with potassium carbonate and stirred for 1 h. The organic layer was separated, saturated with potassium carbonate, and stirred for an additional 3 h. The reaction mixture was then diluted with ether, filtered, and concentrated under reduced pressure. The residue was subjected to flash chromatography with a 25% ethyl acetate–hexane mixture as the eluent to give 1.3 g (70%) of *N*-benzyloxazolidine (**20**). This structure was identical with that of one of the fractions obtained from the reaction of 1 with lithium fluoride.

Reaction of 1 with 3-Hexanone Trimethylsilyl Enol Ether in the Presence of Boron Trifluoride Etherate. A solution containing 500 mg of 1 in 1 mL of methylene chloride was added dropwise to a solution containing 0.7 mL of boron trifluoride etherate in 11 mL of methylene chloride at −78 °C. The reaction mixture was stirred for 10 min, a solution containing 0.65 g of 3-hexanone trimethylsilyl enol ether[34] in 3 mL of methylene chloride was added, and the reaction mixture was stirred at −78 °C for 6 h. The mixture was stirred for an additional 14 h and was poured into water and extracted with methylene chloride. The organic extracts were dried over magnesium sulfate and concentrated under reduced pressure. The residue was subjected to flash chromatography with a 5% ethyl acetate–hexane mixture as the eluent. The major fraction contained 430 mg (70%) of a clear oil, whose structure was assigned as *N*-benzyl-*N*-(2-methyl-3-oxohexyl)-*N*-[(trimethylsilyl)methyl]amine (**23**) on the basis of its spectral properties: IR (neat) 3010, 1720, 1500, 1390, 1140, 1080, 1050, 860, and 720 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.10 (s, 9 H), 0.92–1.2 (m, 6 H), 1.82 (d, 1 H, *J* = 15.0 Hz), 2.05 (d, 1 H, *J* = 15.0 Hz), 2.1–3.0 (m, 5 H), 3.41 (d, 1 H, *J* = 16.5 Hz), 3.64 (d, 1 H, *J* = 16.5 Hz), and 7.32 (s, 5 H); MS, *m/e* 291 (M^+), 217, 206, 91, and 73. Anal. Calcd for $C_{17}H_{29}NOSi$: C, 70.04; H, 10.03; N, 4.80. Found: C, 69.91; H, 10.06; N, 4.79.

Cycloaddition of *N*-Benzyl-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine (1) with Thioacetamide. A solution containing 79 mg of thioacetamide, 0.25 g of 1, and 0.03 g of lithium fluoride in 3 mL of dry acetonitrile was sonicated for 12 h. The reaction mixture was filtered, and the solvent was removed under reduced pressure to give a colorless oil. The crude material was subjected to silica gel chromatography with a 50% ethyl acetate in hexane solution as the eluent. The major component contained 0.24 g (83%) of a colorless oil, whose structure was assigned as thioamide **25** on the basis of its characteristic spectral data: bp 200 °C (0.02 mm); NMR ($CDCl_3$, 90 MHz) δ 0.10 (s, 9 H), 2.12 (s, 2 H), 2.40 (s, 3 H), 3.67 (s, 2 H), 4.45 (d, 2 H, *J* = 4.0 Hz), 7.30 (s, 5 H); IR (neat) 3240, 3060, 1605, 1520, 1450, 1330, 1025, 740, and 700 cm^{-1}. Anal. Calcd for $C_{14}H_{25}N_2SSi$: C, 59.94; H, 8.62; N, 9.99; S, 11.43. Found: C, 59.90; H, 8.59; N, 9.89; S, 11.40.

Reaction of 1 with Benzyl Cyanoformate in the Presence of Lithium Fluoride. A solution containing 500 mg of 1, 340 mg of benzyl cyanoformate, and 65 mg of lithium fluoride in 5 mL of acetonitrile was sonicated for 5 h. The reaction mixture was poured into water and extracted with ether. The combined ethereal extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residue obtained was subjected to flash chromatography with a 10% ethyl

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acetate–hexane mixture as the eluent. The major fraction isolated contained 390 mg (80%) of a clear oil, whose structure was assigned as N-benzyl-N-(cyanomethyl)-N-[(trimethylsilyl)methyl]amine (26).[12] This material was identical in all respects with that obtained from the reaction of N-benzyl-N-[(trimethylsilyl)methyl]amine with 37% aqueous formaldehyde solution in the presence of potassium cyanide.[12] This same material was also obtained when ethyl cyanoformate was used as the trapping agent.

Preparation of N-Benzyl-N-[α-(trimethylsilyl)ethyl]-N-(methoxymethyl)amine (27). To a solution containing 200 mg of a 37% formaldehyde solution in water at 0 °C was slowly added 0.5 g of N-benzyl-N-[α-(trimethylsilyl)ethyl]amine. To this solution was added 0.15 mL of methanol, and the resulting solution was saturated with potassium carbonate. The mixture was stirred for 1 h, and the nonaqueous phase was separated and stirred overnight with an excess of potassium carbonate. The reaction mixture was filtered, and the excess alcohol was removed under reduced pressure to give 0.45 g (95%) of a clear oil, whose structure was assigned as N-benzyl-N-[α(trimethylsilyl)ethyl]-N-(methoxymethyl)amine (27) on the basis of its spectral properties: IR (neat) 3060, 1500, 1460, 1380, 1250, 1070, 920, 840, and 710 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.05 (s, 9 H), 1.14 (d, 3 H, J = 7.0 Hz), 2.30 (q, 1 H, J = 7.0 Hz), 3.09 (s, 3 H), 3.80 (s, 2 H), 3.90 (d, 1 H, J = 9.0 Hz), 4.05 (d, 1 H, J = 9.0 Hz), and 7.1–7.3 (m, 5 H); MS, m/e 251 (M^+) 220, 134, 91, and 73. Anal. Calcd for $C_{14}H_{25}NOSi$: C, 66.88; H, 10.02; N, 5.57. Found: C, 66.13; H, 9.97; N, 6.03.

Cycloaddition of 27 with 1,1-Bis(p-tolylsulfonyl)ethylene in the Presence of Lithium Fluoride. A solution containing 400 mg of 27, 530 mg of 1,1-bis(p-tolylsulfonyl)ethylene, and 50 mg of lithium fluoride in 6 mL of acetonitrile was sonicated for 5 h. The reaction mixture was poured into water and extracted with ether. The combined ether extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a viscous oil. This material was subjected to silica gel chromatography with a 35% ethyl acetate–hexane mixture as the eluent. The resulting solid was recrystallized from methylene chloride–petroleum ether to give 0.45 g (60%) of a white solid (mp 116–117 °C), whose structure was assigned as N-benzyl-2-methyl-3,3-bis(p-tolylsulfonyl)pyrrolidine (28) on the basis of its spectral properties: IR (KBr) 3070, 1620, 1520, 1480, 1370, 1170, 1110, 840, 770, and 730 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 1.35 (d, 3 H, J = 6.7 Hz), 2.26 (ddd, 1 H, J = 9.6, 9.5, and 6.6 Hz), 2.47 (s, 3 H), 2.49 (s, 3 H), 2.54 (t, 1 H, J = 7.3 Hz), 2.64 (ddd, 1 H, J = 16.1, 10.5, and 7.4 Hz), 2.94 (dd, 1 H, J = 9.5 and 6.6 Hz), 3.25 (d, 1 H, J = 13.2 Hz), 3.33 (q, 1 H, J = 6.7 Hz), 4.00 (d, 1 H, J = 13.2 Hz), 7.1–7.4 (m, 9 H), and 7.9–8.0 (m, 4 H); MS, m/e 483 (M^+), 196, 178, 149, and 91; UV (95% ethanol) 230 nm (ε 28700), 262 (2100), and 274 (1500). Anal. Calcd for $C_{26}H_{29}NO_4S_2$: C, 64.57; H, 6.04; N, 2.90. Found: C, 64.46; H, 5.94; N, 2.81.

Cycloaddition of 27 with Thiobenzophenone in the Presence of Lithium Fluoride. A solution containing 500 mg of 27, 400 mg of thiobenzophenone, and 50 mg of lithium fluoride in 6 mL of acetonitrile was sonicated for 5 h. The reaction mixture was poured into water and extracted with methylene chloride. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography with a 5% ethyl acetate–hexane mixture as the eluent. The 360-MHz NMR spectrum ($CDCl_3$) of the major fraction (75%) showed the presence of two regioisomers in a 1.5:1 ratio. All attempts to separate the mixture into its component parts failed. The major isomer was shown to be 3-benzyl-5,5-diphenyl-4-methylthiazolidine (29) on the basis of its NMR spectrum: δ 0.94 (d, 3 H, J = 6.3 Hz), 3.53 (d, 1 H, J = 13.2 Hz), 3.78 (d, 1 H, J = 6.7 Hz), 3.86 (q, 1 H, J = 6.3 Hz), 3.98 (d, 1 H, J = 13.2 Hz), 4.03 (d, 1 H, J = 6.7 Hz), and 7.0–7.5 (m, 15 H). The minor regioisomer was assigned as 3-benzyl-5,5-diphenyl-2-methylthiazolidine (30) on the basis of its NMR spectrum: δ 1.53 (d, 3 H, J = 6.1 Hz), 3.33 (d, 1 H, J = 11.1 Hz), 3.38 (d, 1 H, J = 13.4 Hz), 3.87 (d, 1 H, J = 13.4 Hz), 3.90 (d, 1 H, J = 11.1 Hz), 4.41 (q, 1 H, J = 6.1 Hz), and 7.0–7.5 (m, 15 H).

Reaction of 27 with Methyl Propiolate in the Presence of Cesium Fluoride. A solution containing 280 mg of 27, 0.1 mL of methyl propiolate, and 230 mg of cesium fluoride in 3 mL of anhydrous acetonitrile was heated at 70 °C for 5 h. The cooled solution was poured into water and extracted with ether. The ethereal extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified on the chromatotron unit with a 20% ethyl acetate–hexane mixture as the eluent. The main fraction contained 130 mg of a clear oil, whose structure was assigned as N-benzyl-N-[α-(trimethylsilyl)ethyl]-N-(*trans*-2-carbomethoxyethenyl)amine (31) on the basis of its spectral properties: IR (neat) 3040, 1700, 1610, 1460, 1360, 1150, 800, and 710 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.10 (s, 9 H), 1.19 (d, 3 H, J = 8.0 Hz), 2.67 (q, 1 H, J = 8.0 Hz), 3.47 (s, 3 H), 4.18 (s, 2 H), 4.46 (d, 1 H, J = 13.0 Hz), 7.16 (s, 5 H), and 7.38 (d, 1 H, J = 13.0 Hz). Anal. Calcd for $C_{16}H_{25}NO_2Si$: C, 66.93; H, 8.65; N, 4.81. Found: C, 66.68; H, 8.46; N, 4.87.

The structure of 31 was further verified by an independent synthesis. A solution containing 500 mg of N-benzyl-N-[α-(trimethylsilyl)ethyl]amine[12] and 0.22 mL of methyl propiolate in 5 mL of acetonitrile was heated at 70 °C for 5 h. The reaction mixture was poured into water and extracted with ether. The ethereal extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified on a silica gel column with a 20% ethyl acetate–hexane mixture as the eluent. The major fraction contained 490 mg (70%) of a material whose structure was assigned as N-benzyl-N-[α-(trimethylsilyl)ethyl]-N-(*trans*-2-carbomethoxyethenyl)amine (31). This material was identical with that obtained from the reaction of 27 with methyl propiolate in the presence of cesium fluoride.

Preparation of N-Benzyl-N-(α-methoxybenzyl)-N-[(trimethylsilyl)methyl]amine (33). To a solution containing 0.55 mL of benzaldehyde in 0.22 mL of methanol was added 1.0 g of N-benzyl-N-[(trimethylsilyl)methyl]amine.[12] After the solution was stirred for 10 min, it was saturated with solid potassium carbonate and was sitrred overnight. The reaction mixture was filtered, and the excess solvent was removed under reduced pressure. The 90-MHz NMR spectra ($CDCl_3$) showed that N-benzyl-N-(phenylmethoxymethyl)-N-[(trimethylsilyl)methyl]-amine (33) was present in a 2.8:1 ratio with starting material: NMR ($CDCl_3$, 90 MHz) δ 0.10 (s, 9 H), 1.89 (d, 1 H, J = 15.0 Hz), 2.20 (d, 1 H, J = 15.0 Hz), 3.32 (s, 3 H), 3.63 (s, 2 H), 4.83 (s, 1 H), and 7.0–7.3 (m, 10 H). Due to the ready hydrolysis of this compound, the mixture was used directly in the next step without purification.

Cycloaddition of N-Benzyl-N-(α-methoxybenzyl)-N-[(trimethylsilyl)methyl]amine (33) with Thiobenzophenone in the Presence of Lithium Fluoride. A solution containing 320 mg of 33, 220 mg of thiobenzophenone, and 30 mg of lithium fluoride in 6 mL of acetonitrile was sonicated for 5 h. The reaction mixture was poured into water and extracted with methylene chloride. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. This residue was purified by silica gel chromatography with a 5% ethyl acetate–hexane mixture as the eluent. The 360-MHz NMR spectrum ($CDCl_3$) of the major fraction (60%) showed the presence of two regioisomers in a 3:2 ratio. The major isomer was shown to be N-benzyl-4,5,5-triphenylthiazolidine (35) on the basis of its NMR spectrum: δ 3.35 (d, 1 H, J = 13.5 Hz), 3.72 (d, 1 H, J = 13.5 Hz), 3.87 (d, 1 H, J = 6.7 Hz), 4.17 (d, 1 H, J = 6.7 Hz), 5.28 (s, 1 H), and 7.0–7.6 (m, 20 H). The minor isomer was assigned as N-benzyl-2,5,5-triphenylthiazolidine (36) on the basis of its NMR spectrum: δ 3.14 (d, 1 H, J = 10.5 Hz), 3.18 (d, 1 H, J = 13.2 Hz), 3.86 (d, 1 H, J = 13.2 Hz), 4.05 (d, 1 H, J = 10.5 Hz), 5.12 (s, 1 H), and 7.0–7.6 (m, 20 H). All attempts to separate the mixture into its component parts failed. These same two compounds were formed in the same ratio from the reaction of 37 (vide infra) with LiF in the presence of thiobenzophenone.

Preparation of N-Benzyl-N-(methoxymethyl)-N-[phenyl(trimethylsilyl)methyl]amine (37). To a solution containing 1.51 g of a 37% aqueous formaldehyde solution at 0 °C was slowly added 5.0 g of α-(trimethylsilyl)dibenzylamine.[35] To this solution

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was added 1.65 mL of methanol, and the resulting mixture was saturated with potassium carbonate. The mixture was stirred for 1 h, and the organic phase was separated and stirred overnight with an excess of potassium carbonate. The reaction mixture was diluted with ether, filtered, dried over potassium carbonate, and concentrated under reduced pressure to give 5.2 g (89%) of a clear oil, whose structure was assigned as *N*-benzyl-*N*-(methoxymethyl)-*N*-[phenyl(trimethylsilyl)methyl]amine (**37**) on the basis of its spectral properties: IR (neat) 3060, 1710, 1650, 1600, 1450, 1070, 760, and 700 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 0.10 (s, 9 H), 3.15 (s, 3 H), 3.65 (s, 1 H), 3.71 (d, 1 H, J = 13.2 Hz), 3.78 (d, 1 H, J = 13.2 Hz), 4.00 (d, 1 H, J = 9.3 Hz), 4.15 (d, 1 H, J = 9.3 Hz), and 7.1–7.5 (m, 10 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 0.17, 54.5, 56.9, 66.6, 85.8, 126.8, 127.3, 128.5, 129.8, 130.2, and 132.3; MS, m/e 313 (M^+), 267, 196, 178, and 91. Anal. Calcd for $C_{19}H_{27}NOSi$: C, 72.79; H, 8.68; N, 4.47. Found: C, 72.83; H, 8.70; N, 4.45.

Cycloaddition of 37 with 1,1-Bis(*p*-tolylsulfonyl)ethylene in the Presence of Lithium Fluoride. A solution containing 500 mg of **37**, 540 mg of 1,1-bis(*p*-tolylsulfonyl)ethylene,[30] and 80 mg of lithium fluoride in 6 mL of acetonitrile was sonicated for 5 h. The reaction mixture was poured into water and extracted with ether. The combined ether extracts were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting oil was subjected to silica gel chromatography with a 35% ethyl acetate–hexane mixture as the eluent. The oil that was obtained was recrystallized from methylene chloride–petroleum ether to give 0.13 g (15%) of a white solid, mp 187–188 °C, whose structure was assigned as *N*-benzyl-2-phenyl-3,3-bis(*p*-tolylsulfonyl)pyrrolidine (**34**) on the basis of its spectral properties: IR (KBr) 3050, 1600, 1495, 1330, 1150, 1020, 880, 770, and 700 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 1.87 (ddd, 1 J, J = 5.8, 8.8 and 11.2 Hz), 2.58 (dd, 1 H, J = 5.8 and 14.6 Hz), 3.03 (dd, 1 H, J = 7.5 and 8.8 Hz), 3.05 (d, 1 H, J = 13.4 Hz), 3.17 (ddd, 1 H, J = 7.5, 11.2, and 14.6 Hz), 3.82 (d, 1 H, J = 13.4 Hz), 4.43 (s, 1 H), and 7.1–8.0 (m, 18 H); MS, m/e 545 (M^+), 415, 401, 167, 149, and 91; UV (95% ethanol) 232 nm (ϵ 10400). Anal. Calcd for $C_{31}H_{31}NO_4S_2$: C, 68.23; H, 5.73; N, 2.57. Found: C, 67.94; H, 5.77; N, 2.53. This same material was formed from the reaction of silyl methoxy amine **33** with lithium fluoride in the presence of 1,1-bis(*p*-tolylsulfonyl)ethylene.

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Registry No. 1, 93102-05-7; 3, 97998-53-3; 4, 87813-05-6; 5, 87813-06-7; 6, 101767-83-3; 7, 105518-91-0; 8, 105518-92-1; 9, 105518-93-2; 10, 104143-95-5; 11, 105518-94-3; 12, 105518-95-4; 13, 105537-40-4; 14, 105518-96-5; 15, 105518-97-6; 16, 105518-98-7; 17, 105518-99-8; 18, 105519-00-4; 19, 1483-42-7; 20, 13657-16-4; 23, 105537-41-5; 25, 105519-01-5; 26, 87813-07-8; 27, 105519-02-6; 28, 105519-03-7; 29, 105519-04-8; 30, 105537-42-6; 31, 105519-05-9; 33, 105519-06-0; 34, 105519-07-1; 35, 105519-08-2; 36, 105519-09-3; 37, 105519-10-6; 38, 105519-11-7; 39, 105519-12-8; $TMSCH_2NHCH_2Ph$, 53215-95-5; CsF, 13400-13-0; LiF, 7989-24-4; $ZnCl_2$, 7646-85-7; $PhCH_2OCOCN$, 5532-86-5; $HC{\equiv}CCO_2CH_3$, 922-67-8; *N*-benzyl-*trans*-3,4-dicyanopyrrolidine, 87813-02-3; 2,6-dioxo-1-phenyl-4-benzyl-1,4-diazobicyclo[3.3.0]octane, 93102-03-5; *o*-vinylbenzyl chloride, 22570-84-9; benzaldehyde, 100-52-7; fumaronitrile, 764-42-1; *N*-phenylmaleimide, 941-69-5; dimethyl fumarmate, 624-49-7; dimethyl maleate, 624-48-6; phenyl vinyl sulfine, 5535-48-8; *N*-benzyl-*N*-[(trimethylsilyl)methyl)]-*N*-[(β-(phenylsulfonyl)ethyl)]amine, 105519-13-9; 1,1-bis(*p*-tolylsulfonyl)ethylene, 39837-38-2; benzophenone, 119-61-9; acetone, 67-64-1; thiobenzophenone, 1450-31-3; ethoxymethacrolein, 62055-46-3; 5-hexenal, 764-59-0; [(trimethylsilyl)methyl]amine, 18166-02-4; *N*-(*o*-vinylbenzyl)-*N*-[(trimethylsilyl)methyl]amine, 105519-14-0; *N*-benzylaziridine, 1074-42-6; *N*-benzylmethylamine, 103-67-3; *N*-benzylethanolamine, 104-63-2; 3-hexanone trimethylsilyl enol ether, 105519-15-1; thioacetamide, 62-55-5; *N*-benzyl-*N*-[(α-trimethylsilyl)ethyl)]amine, 97998-46-4; (trimethylsilyl)dibenzylamine, 70601-93-3.

Convenient Syntheses of Precursors of Silylated 1,3-Dienes

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Several 2- or 3-silylated 3-sulfolenes have been prepared from 3-sulfolenes by the direct deprotonation/substitution sequence. These sulfolenes serve as the stable precursors for the silylated 1,3-dienes and can be used directly in Diels–Alder reactions without isolation of the diene intermediates.

The Diels–Alder reaction of a silylated 1,3-diene with a dienophile results in the formation of either a cyclic vinylsilane or a cyclic allylsilane.[1] Both vinylsilanes and allylsilanes are useful functionalities and find broad applications in organic synthesis.[2] For this reason, the preparation of silylated 1,3-dienes[1,3] and the regio- and stereoselectivity of their cycloaddition reactions[1] have received much attention from organic chemists. Literature methods for the preparation of 2-silylated 1,3-dienes normally involve the use of 1,4-difunctionalized 2-butynes,[3a-c] the catalyzed cross-coupling of silylated alkenes,[3d,e] and the LAH reduction of silylated allenic alcohols,[3f] while those for 1-silylated 1,3-dienes involve the condensation reactions of silylated carbanions with carbonyl compounds,[1a,d,3g] the Wittig reaction of silylated acrolein,[1c] and the hydroalumination of silylated 1,3-diynes.[3g] These procedures either are multistep or require starting materials that are not readily accessible. In addition, the silylated dienes are often difficult to purify because of their tendency to decompose upon distillation and because they readily polymerize upon long-term storage. Herein we report a very convenient method for the preparation of the stable precursors for the silylated 1,3-dienes, the silylated 3-sulfolenes, via the direct de-

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