Synthesis and Reactivity of *N*-[Bis(trimethylsilyl)methyl]heterocumulenes

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A number of *N*-heterocumulenes bearing the $(Me_3Si)_2CH$ (BSM) substituent adjacent to the terminal nitrogen atom of the heterocumulene function, namely BSM-N=C=O (**2**), BSM-N=C=S (**3**), BSM-N=C=NR (**4**: R = BSM; **5**: R = C_6H_5), BSM-N=C=CR_1R_2 (**9a**: $R_1 = R_2 = C_6H_5$; **9b**: R_1 = H, R_2 = $SiMe_3$; **10**: $R_1 = R_2 = CH_3$; **12**: R_1 = H; $R_2 = CH_3$), and BSM-N=S=O (**14**), have been synthesized. The synthetic utility of the BSM-N-substituted heterocumulenes has been explored through the creation of a carbanion center at the α position relative to nitrogen. In particular, the following reactions have been studied: (i) the nucleophilic addition of MeLi to compounds **2** and **5**, (ii) the MeLi-induced deprotonation of ketene imines **9a,b** (this investigation includes the study of the regiochemical output of the addition of electrophiles (H_2O, MeI, Me_2CHI) to the resulting 1,3-dipoles; and (iii) the TBAF-induced desilylation of compounds **2** and **9a** followed by reaction with benzaldehyde.

The functional group $(Me_3Si)_2CHN$ (BSM-N) has attracted the interest of many research groups due to its versatility in organic synthesis. In fact, the BSM-N= substituent presents three potential reactive sites: (i) The CH ligand can give, in the presence of strong bases, the α-amino carbanion $(Me_3Si)_2C^-N$= containing two silicon atoms. (ii) The SiC ligand can give a different α-amino carbanion Me_3SiHC^-N= containing only one silicon atom, obtained *via* fluoride-induced desilylation. (iii) Finally, the nitrogen atom of the amino function can be involved in single or multiple bonds. For example, we have recently demonstrated that the presence of the BSM substituent in the framework of azomethine derivatives [$(Me_3Si)_2CHN=CR_1R_2$] conveys unique and interesting features to their reactivity with electrophilic reagents through the formation of an intermediate 2-azaallylmetallic derivative by hydrogen metal exchange.[1] At present, the BSM substituent is mostly involved in the chemistry of amino derivatives [$(Me_3Si)_2CHNR_1R_2$][2a,b] and of azomethine derivatives [$(Me_3Si)_2CHN=CR_1R_2$].[2a,3a-d]

We have initiated a research program which examines the synthesis and reactivity of a number of *N*-heterocumulenes bearing the $(Me_3Si)_2CH$ substituent (BSM) adjacent to the terminal nitrogen atom of the heterocumulene function, namely: BSM-N=C=O, BSM-N=C=S, BSM-N=C=CR_1R_2, BSM-N=C=NR, and BSM-N=S=O. These studies will be directed toward the development of new methodologies for the synthesis of heterocycles by coupling the synthetic potentiality of the BSM-N= function, as described above, with the typical reactivity of the heterocumulenes in cycloaddition reactions.

Results and Discussion

(A) Synthesis of BSM-N-heterocumulenes. (1) Synthesis of BSM-N=C=O (2) and of BSM-N=C=S (3). Syntheses of BSM-N=C=O (**2**) and BSM-N=C=S (**3**) have been reported in the literature by the following methods. The isocyanate **2** is synthesized by reaction of bis(trichloromethyl) carbonate and BSM-NH_2[2a] (procedure A, Scheme 1, step i), while the isothiocyanate **3** is prepared by addition of sulfur to bis(trimethylsilyl)methyl isocyanide (procedure A, Scheme 1, step ii).[4] We preferred to develop, according to Staudinger's protocol,[5] a straightforward, one-step procedure starting from BSM-iminophosphorane (**1**), which is easily available from BSM-N_3[2b] and PPh_3 (procedure B, Scheme 1). The addition of CO_2 and CS_2 at 25 °C to the phosphorane **1** gave high yields of **2** and of **3**, respectively, *via* a Wittig-type reaction probably involving the formation of an unstable betaine intermediate that rapidly eliminated Ph_3P=O and Ph_3P=S.[6]

(2) Synthesis of BSM-N=C=N-BSM (4) and BSM-N=C=NC_6H_5 (5). The imino phosphorane route was also used for the synthesis of the BSM-substituted carbodiimides **4** and **5**. The symmetrically BSM-substituted carbodiimide **4** (Scheme 2) was obtained by reaction of BSM-phosphorane **1** with BSM-N=C=O *via* a Wittig-

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(1) Ricci, A.; Guerrini, A.; Seconi, G.; Mordini, A.; Constantieux, T.; Picard, J.-P.; Aizpurua, J.-M.; Palomo, C. *Synlett* **1994**, 955–957.

(2) (a) Grelier, S. Thesis, Univ. Bordeaux I, 1991, no. 633, p 62. (b) Picard, J. P.; Grelier, S.; Donogues, J.; Aizpurua, J. M.; Palomo, C. *J. Organomet. Chem.* **1991**, *419*, C1–C4.

(3) (a) Lasarte, J.; Palomo, C.; Picard, J.-P.; Donogues, J.; Aizpurua, J.-M.; Palomo, C. *J. Chem. Soc. Chem. Commun.* **1989**, 72–74. (b) Capperucci, A.; Ricci, A.; Seconi, G.; Donogues, J.; Grelier, S.; Picard, J.-P.; Aizpurua, J.-M.; Palomo, C. *J. Organomet. Chem.* **1993**, *458*, C1. (c) Palomo, C.; Aizpurua, J.-M.; Garcia, J.-M.; Picard, J.-P.; Donogues, J. *Tetrahedron Lett.* **1990**, *31*, 1921–1924. (d) Palomo, C. ; Aizpurua, J.-M.; Legido, M.; Picard, J.-P.; Donogues, J. ; Constantieux, T. *Tetrahedron Lett.* **1992**, *33*, 3903–3906.

(4) Hirao, T.; Yamada, A.; Ohshiro, Y.; Agawa, T. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 126–127.

(5) Staudinger's methodology has been used for synthesizing (trimethylsilyl)methyl isothiocyanate. See ref 14b.

(6) The syntheses of compounds **2** and **3** *via* iminophophorane **1** employ bis(trimethylsilyl)chloromethane as the starting material instead of the less expensive trimethylsilyl cyanide, which is used in the previously known methodologies.[2a,4] Even so, Staudinger's protocol is more useful since **2** and **3** are prepared in 61% and 62% overall yields, respectively, with a three-step protocol (Scheme 1). The isocyanate **2** is prepared from trimethylsilyl cyanide in 40% overall yields with a four-step procedure, and the isothiocyanate **3** is prepared in a 10–20% overall yield with a seven-step procedure. It is also worth noting that the reductive silylation of BSM-CN requires large amounts of very expensive HMPA (HMPA:BSM-CN = 10:1), while Staudinger's protocol uses this solvent in the synthesis of BSM-N_3, but in minor amounts (HMPA:BSM-Cl = 2.8:1).

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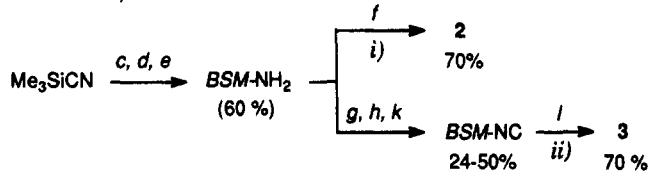
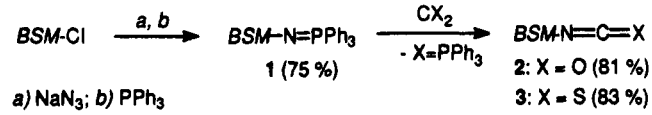
Scheme 1

Procedure A)



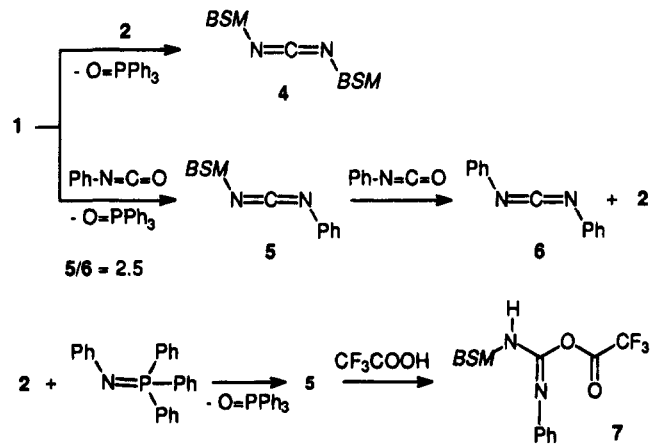
c) Me_3SiCl / Li; *d)* MeOH/Me_3SiCl; *e)* NaOH; *f)* $1/3(Cl_3CO)_2C{=}O$
g) HCOOH / - H_2O; *h)* BuLi / Me_3SiCl; *k)* $POCl_3$ / Py; *l)* S_X

Procedure B)



a) NaN_3; *b)* PPh_3

Scheme 2



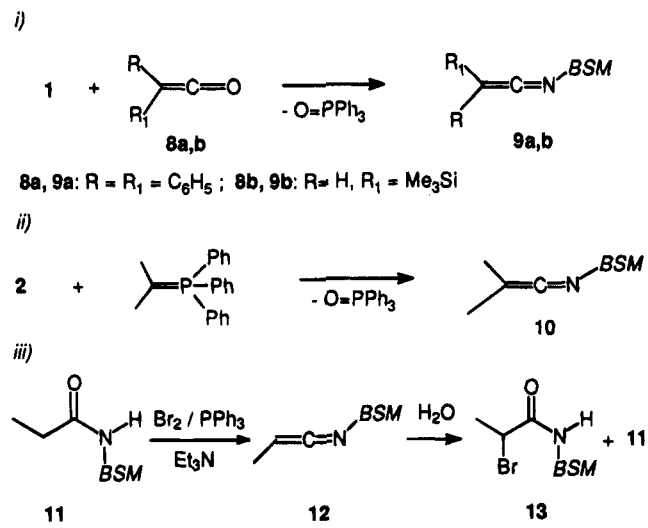
type reaction. However, the synthesis of the unsymmetrically substituted BSM-N=C=NC_6H_5 (**5**) was performed using two different procedures: (i) Compound **5** was obtained in a 2.5:1 mixture with the symmetrically substituted *N,N'*-diphenylcarbodiimide (**6**) by reaction of **1** with phenyl isocyanate. Compound **6** was the result of a cycloreversion of an unstable 1,3-oxazetidine, which was formed by competitive 1,2-cycloaddition of unreacted phenyl isocyanate to the *N*-phenyl-substituted C=N bond of **5**.[7] (ii) Compound **5** was obtained as the only product of the reaction of isocyanate **2** and tetraphenyl-substituted iminophosphorane.[8] Interestingly, the protonation of the asymmetrically substituted carbodiimide **5** by CF_3-COOH occurs at the electronically activated imino nitrogen which bears the geminally silylated carbon atom, regioselectively, affording the corresponding 3-phenyl-2-(trifluoroacetyl)isourea **7**. In contrast, our attempts to generate the carbodiimidium salts, by reaction of **5** in refluxing MeI, failed.[9] This reaction led exclusively to oligomers.

(7) In principle, a possible addition of phenyl isocyanate to the BSM-substituted C=N bond of carbodiimide **5** could afford a regioisomeric 1,3-oxazetidine whose cycloreversion leads to the starting carbodiimide.

(8) It is worth noting that a competitive 1,2-addition of unreacted BSM-N=C=O to the C=N bond of **5** which bears the phenyl substituent should afford an oxazetidine whose cycloreversion leads to the starting carbodiimide **5**, while the addition to the more sterically hindered C=N bond which bears the BSM substituent should afford a regioisomeric oxazetidine whose cycloreversion leads to the symmetrically substituted carbodiimide **4**. The formation of this side product was not observed.

(9) A similar procedure was used by Scheffold et al. for the synthesis of *N*-alkyl dicyclohexylcarbodiimidium salts. See: Scheffold, R.; Saladin, E. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 229–231.

Scheme 3



(3) Synthesis of BSM-N-ketene Imines (BSM-N=C=CR_1R_2) (9a,b, 10, and 12). Three different protocols were successfully attempted for the synthesis of BSM-N substituted ketene imines. One method (i, Scheme 3) employs iminophosphorane **1** and thermally stable ketenes, such as the diphenylketene **8a** (R = R_1 = C_6H_5) or the silylketene **8b** (R = H, R_1 = Me_3Si) as the partners.[10] This method affords the corresponding betaines which rapidly decompose at 25 °C. However, while ketene imine **9a** was obtained in high yields, ketene imine **9b** was obtained in variable amounts due to a competitive formation of a 2:1 adduct (two molecules of ketene **8b** and one molecule of **1**). Yields of **9b** depended on the reaction conditions. For instance, when **8b** and **1** were mixed in a 2:1 ratio, the reaction gave rise to **9b** in 12% yield with respect to **1**. The yields of the product increased when the fixed amount of the intermediate betaine present during the reaction was maintained at a very low level by the very slow addition of a 60% molar excess solution of ketene into a solution of the iminophosphorane. According to this procedure, the ketene imine **9b** was obtained in 56% yield with respect to **1**. The distillation of the crude reaction mixture produced a substantial decomposition of **9b**, which was obtained in 42% yield. This protocol failed to give the ketene imine **10** when the unstable dimethylketene was used as the starting material. This ketene imine was obtained in moderate yield (41%) with a different method (ii, Scheme 3),[11] by reacting the salt-free isopropylidenetriphenylphosphorane with BSM-N=C=O. The reaction, performed at 25 °C, stopped at the betaine stage. The ketene imine **10** was directly distilled under vacuum during the decomposition of the betaine at 120 °C. Attempts to synthesize the *C*-methyl monosubstituted ketene imine **12** with the same protocol, by reacting ethylidenetriphenylphosphorane and BSM-NCO, failed.[12] Instead, compound **12** was synthesized by reacting the amide **11** with bromine, PPh_3, and Et_3N (iii, Scheme 3). It is worth

(10) Staudinger, H.; Meyer, J. *Ber.* **1920**, *53*, 72–76.

(11) Froyen, P. *Acta Chem. Scand.* **1974**, *B 28*, 586–588 and references therein.

(12) The reaction of ethylidenetriphenylphosphorane and BSM-NCO affords the betaine $Ph_3P^+CHMeC(O^-){=}NCH(SiMe_3)_2$. This betaine spontaneously rearranges to the ylide $Ph_3P{=}CMeC(O)NHCH(SiMe_3)_2$ *via* a 1,3-migration of the hydrogen atom to the nitrogen. Similar results were obtained by Trippett and Walker[13] in the reaction of phenyl isocyanate and ylides containing an α-atom.

(13) Trippett, S.; Walker, D. *J. Chem. Soc.* **1959**, 3874–3876.

Scheme 4

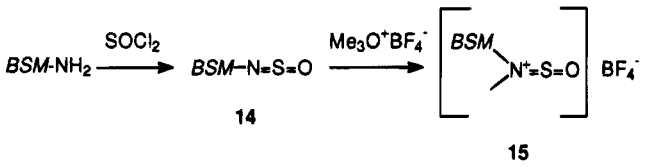
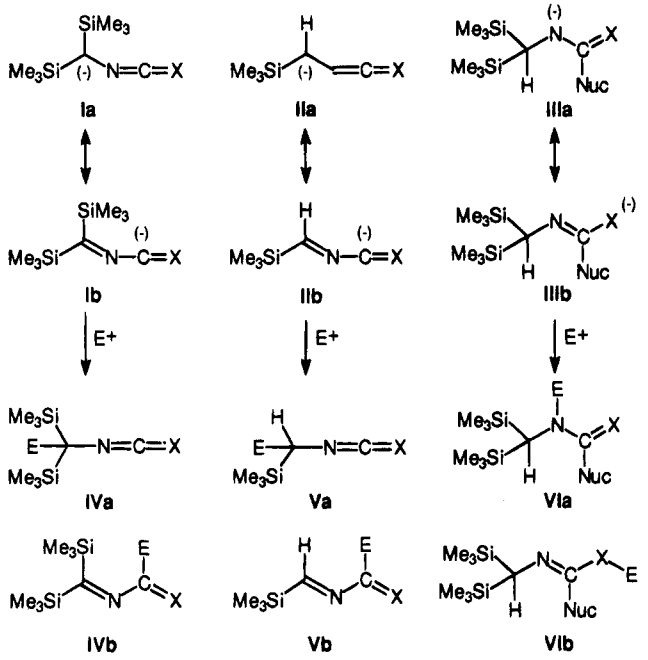


Chart 1

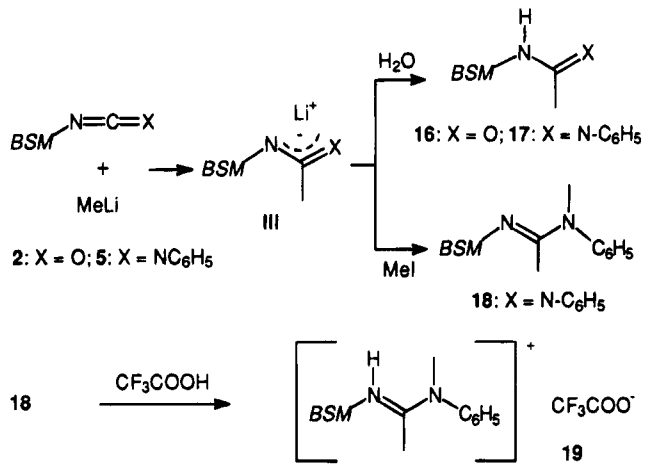


noting that a 3-fold excess of bromine/PPh_3 was required for total consumption of **11**. The ketene imine was detected spectroscopically by the IR spectrum of the crude reaction mixture which exhibited the characteristic cumulene absorption at 2010 cm^{-1}. Our attempts to isolate the ketene imine **12** were frustrated, due to its decompostion during the workup. However, the addition of H_2O to the crude reaction mixture caused an instantaneous hydration and bromination of **12** with the formation of the starting amide **11** and of the α-bromo amide **13** in a 1:3 ratio (65% overall yields with respect to the starting amide).

(4) Synthesis of BSM-N=S=O (14). BSM-N=S=O was prepared by the addition of $SOCl_2$ to BSM-NH_2 in the presence of Et_3N (Scheme 4). BSM-N=S=O is stable at −20 °C and can be stored under an argon atmosphere. The reaction of trimethyloxonium tetrafluoroborate with the N-BSM sulfinylamine **14** in CH_3NO_2 gave the corresponding methyl sulfinylimmonium salt **15**. A possible use of these compounds as the dienophile partners in heterocycloaddition reactions is under investigation.

B. Reactivity of BSM-N-heterocumulenes. The main target of this investigation was to enhance the synthetic utility of heterocumulenes by creating a carbanion center at the α position relative to the nitrogen. Such metalation can be achieved by reacting the BSM-N-substituted heterocumulenes with strong bases or by cleavage of a carbon−silicon bond by a fluoride ion. In both cases an azomethine ylide 1,3-dipole of nonstabilized type is produced, containing one or two silicon atoms, respectively (**Ia,b** and **IIa,b**, Chart 1). The utility of nonstabilized azomethine ylides in heterocyclic synthesis has been recently demonstrated.[14] In regard to the BSM-N-heterocumulenes, the use of metalated

Scheme 5



$Me_3SiCHN{=}C{=}S^-$, obtained by fluoride-induced desilylation of BSM-N=C=S, in a 1,3-dipolar addition reaction with benzaldehyde and imines has been reported.[15] Finally, it is worth noting that the addition of nucleophiles at the central atom of the heterocumulene function may compete with hydrogen abstraction. This gives rise to another nonstabilized 1,3-dipole (**IIIa,b**). The addition of electrophiles to the 1,3-dipoles **I**−**III** affords two possible regioisomers with structures **IVa**−**VIa** and **IVb**−**VIb**. Here we report the results of our studies on the regioselectivity of the reactions of a selected number of BSM-N-heterocumulenes with MeLi, which afford 1,3-dipoles of type **I** and **III**, followed by the addition of electrophiles to the resulting reaction mixture. We also report the results of our studies on the regioselectivity of the addition of benzaldehyde and of benzylideneaniline to 1,3-dipoles of type **II**.

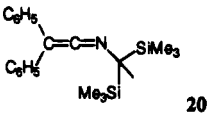
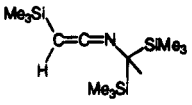
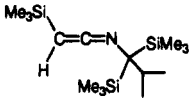
(1) Nucleophilic Addition of MeLi to BSM-N=C=O (2) and BSM-N=C=NC_6H_5 (5): Formation of Type III 1,3-Dipoles. The reaction of MeLi with BSM-N=C=O (**2**) and BSM-N=C=NC_6H_5 (**5**) involved the nucleophilic addition of the methyl group to the central carbon atom of the heterocumulene with the consequent formation of the corresponding type **III** 1,3-dipoles. The addition of H_2O to the 1,3-dipoles afforded the regioisomer of type **VIa** (Scheme 5), namely the amide **16** and the amidine **17**. The addition of MeI to the 1,3-dipole, obtained from the addition of MeLi to the carbodiimide **5**, afforded the regioisomer of type **VIb**, namely the amidine **18**. The structural assignment of **18** was based on the ^1H NMR spectrum of the corresponding trifluoroacetate amidinium salt **19**. In fact, it is well known that proton addition occurs exclusively at the imino nitrogen of the amidines, leading to a symmetrical amidinium ion which is stabilized by resonance.[16] In our case, the hydrogen atom of the amidinium salts derived from **18** was assigned to the nitrogen atom which

(14) For an exhaustive review on this topic see: Vedejs, E.; Fredeick, G. W. *Chem. Rev.* **1986**, *89*, 941−955 and references therein. For alternate ways to generate nitrile ylides by desilylation methods see, for example: (a) Tsuge, O.; Kanemasa, S; Matsuda, K. *Chem. Lett.* **1985**, 1411−1414. (b) Padwa, A.; Gasdaska, J. R.; Haffmanns, G.; Rebello, H. *J. Org. Chem.* **1987**, *52*, 1027−1035. (c) Achiwa, K.; Imai, N.; Motoyama, T.; Sekiya, M. *Chem. Lett.* **1984**, 2041−2044.

(15) Hirao, T.; Yamada, A.; Hayashi, K.; Ohshiro, Y.; Agawa, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1163−1167.

(16) (a) Hafelinger, G. In *The Chemistry of Amidine and Imidates*; Patai, S., Ed.; Interscience Publ.: London, 1975; Chapter 1, pp 2−79 and references therein. (b) Fodor, G.; Phillips B. A. In *The Chemistry of Amidine and Imidates*; Patai, S., Ed.; Interscience Publ.: London, 1975; Chapter 2, pp 85−155 and references therein.

Table 1. Reaction of BSM-N-ketene Imines 9a and 9b with MeLi Followed by Reaction with Electrophiles

Reagent	Electrophile	Product	Yield[a]
9a	MeI	 **20**	66
9b	MeI	 **21**	65
9b	Me_2CHI	 **22**	54

[a] Determined on the crude reaction mixture by ^1H NMR.

contained the BSM substituent due to a coupling between the NH and the vicinal CH of the BSM substituent (J = 10.6 Hz). Interestingly, MeI and H_2O add with different regiochemistry to the 1,3-dipole obtained from the addition of MeLi to the carbodiimide **5**. It should be noted that the *N,N'*-disubstituted amidine **17** may exhibit tautomerism[16] so that proton addition to the 1,3-dipole may occur initially on the nitrogen atom of the *N*-phenyl substituent and then tautomerize. On the other hand, the *N*-trisubstituted amidines, as compound **18**, do not display tautomerism. In this case, the steric effect of the BSM substituent plays a pivotal role in the regioselectivity of the amidine formation since a prevalence of the steric over the electronic effects is observed in the addition of the bulkier electrophile, MeI. As far as the formation of amidine **17** is concerned, our attempts to show, by ^1H NMR, the existence of the two tautomers after quenching the 1,3-dipole with H_2O at −40 °C failed. Only the regioisomer **17** was observed. As a consequence, the product distribution may be explained either as the result of a kinetic control of the site of addition which occurs at the nitrogen atom bearing the BSM substituent, *i.e.*, at the electronically activated site,[1] or of a very fast rate constant for tautomerism, this depending on the relative electronegativities of the two substituents at the nitrogen atoms.[16b] In our case the effects of the phenyl and of the BSM substituents are parallel, thus favoring the tautomer **17**.

(2) MeLi-Induced Deprotonation of Ketene Imines BSM-N=C=C(C_6H_5)$_2$ (9a) and BSM-N=C=CH-SiMe$_3$ (9b): Formation of Type I 1,3-Dipoles. Hydrogen−metal exchange in the BSM substituent requires the presence of a strong base.[1] We observed a regioselective deprotonation of ketene imines **9a,b** in the presence of MeLi, which afforded the corresponding azaallylic metal derivatives of type **I**. These species further reacted with alkyl halogenides (MeI and Me_2CHI) at the geminally silylated carbon atom, i.e., the electronically activated site, to afford the regioisomers of type **IVa**, namely the ketene imines **20**−**22** (Table 1). Interestingly, the regiochemistry appeared to be unaffected by mono, and disubstitution at the terminal carbon of the starting ketene imine. The formation of products deriving from an addition of MeLi to the central carbon atom of the ketene imines was not observed. Our attempts to deprotonate ketene imines **9a,b** with *n*-butylitium failed, probably due to steric effects.

(3) TBAF-Induced Desilylation of BSM-N=C=O (2), BSM-N=C=S (3), and Ketene Imine 9a: Formation of Type II 1,3-Dipoles. As mentioned in the introduction, the fluorodesylilation of BSMA-heterocumulenes allows for the synthesis of metalated heterocumulenes, i.e., of 1,3-dipoles of the general formula **II**, that are attractive building blocks for the synthesis of a variety of interesting 5-membered ring heterocycles. A detailed investigation on the reactivity of these 1,3-dipoles with dipolarophiles is beyond of the scope of this paper.[17] Here we report, as selected examples of this protocol, the cycloaddition of the 1,3-dipoles of **2**, **3**, and **9a** with heterodipolarophiles, such as benzaldehyde and benzylideneaniline. These reactions constitute a methodology for the syntheses of oxazole and imidazole derivatives. In particular, aldehydes may afford oxazolidin-2-ones by reaction with the 1,3-dipole of **2**, oxazolidine-2-thiones with that of **3**, and 1,3-oxazolines with 1,3-dipoles of BSM-*N*-ketene imines. The corresponding imidazole derivatives are obtained in the reaction with imines. These heterocycles may have utility as synthetic or pharmaceutical intermediates.[18] When the fluorodesilylation is performed in the presence of carbonyl compounds, *N*-vinylheterocumulenes can be competitively obtained *via* a Peterson-olefination.[3a-d,19] For instance, Hirao et al. report that BSM-N=C=S affords a mixture of *cis* and *trans*-styryl isothiocyanate, *via* a Peterson olefination, and 5-phenyl-4-(trimethylsilyl)oxazolidine-2-thione, *via* 1,3-dipolar cycloaddition, in a 6:1 isothiocyanate/oxazolidine ratio (37% overall yields).[15] Ketene imine **9a** and BSM-N=C=O behaved differently from BSM-N=C=S when they were subjected to a TBAF-induced reaction with benzaldehyde. In fact, **2** and **9a** both gave a mixture of the corresponding cycloadducts, *cis*- and *trans*-5-phenyl-4-(trimethylsilyl)oxazolidin-2-one (*cis*- and *trans*-**23**, *cis/trans* = 1:1) and *cis*- and *trans*-2-benzhydryl-4-(trimethylsilyl)-5-phenyl-1,3-oxazoline (*cis*- and *trans*-**25**, *cis/trans* = 1:2), respectively, *via* a 1,3-dipolar cycloaddition (Scheme 6). The formation of styryl isocyanates and of styryl ketene imines was not observed. In addition, BSM-N=C=O gave variable amounts of benzylidene-BSMA (**24**).[20] The **24/23** product distribution is strictly dependent on the reaction conditions. For instance, a **24/23** ratio of 2.5:1 was found when the isocyanate was slowly added to a THF solution of benzaldehyde and TBAF, this ratio being reduced to 0.36:1 when the TBAF was added to a 1:1 mixture of the reagents. In this case *cis*, and *trans*-**23** were obtained in 34% overall yield.

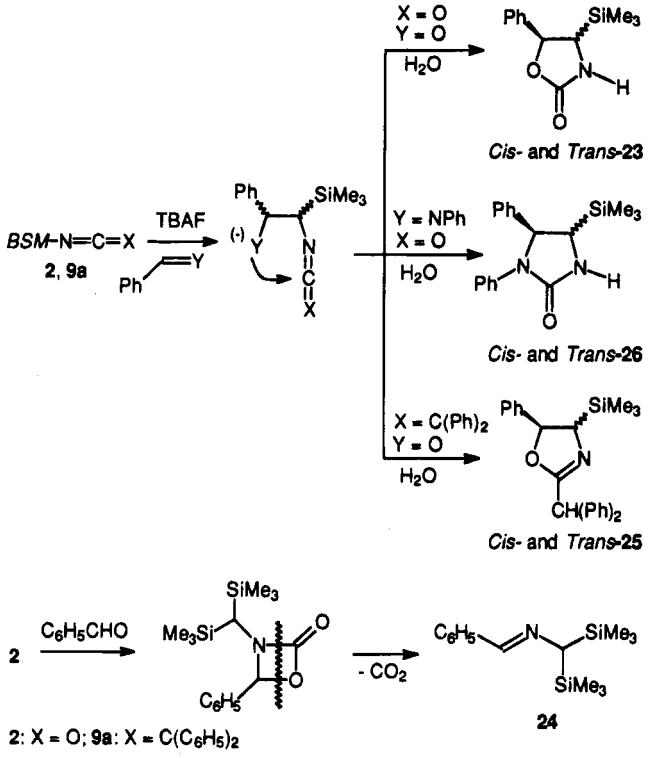
(17) For the use of electrophilically activated dipolarophiles as the partners in cycloaddition reactions with dipoles generated by desylilation of BSM-N substituted imines in the presence or absence of acyl chlorides, see ref 2a.

(18) (a) Selected examples, taken from the literature,[18b] of drugs containing the oxazolidine and the imidazolidine ring, as compounds **23**, **26**, and **28**, are as follows. 2-Oxazolidinones: mephenoxalone (tranquilizer), metaxalone (relaxant), and fenmetazole (antidepressant). 2-Imidazolidinones: nifurimide (antibacterial), niridazole (antischistosomal). 2-Imidazolidinethione: mipimazole (antithyroidal). (b) *Comprehensive Medicinal Chemistry*; Drayton, C. J., Ed.; Pergamon Press: Oxford, U.K. 1990; Vol. 6, pp 237−965.

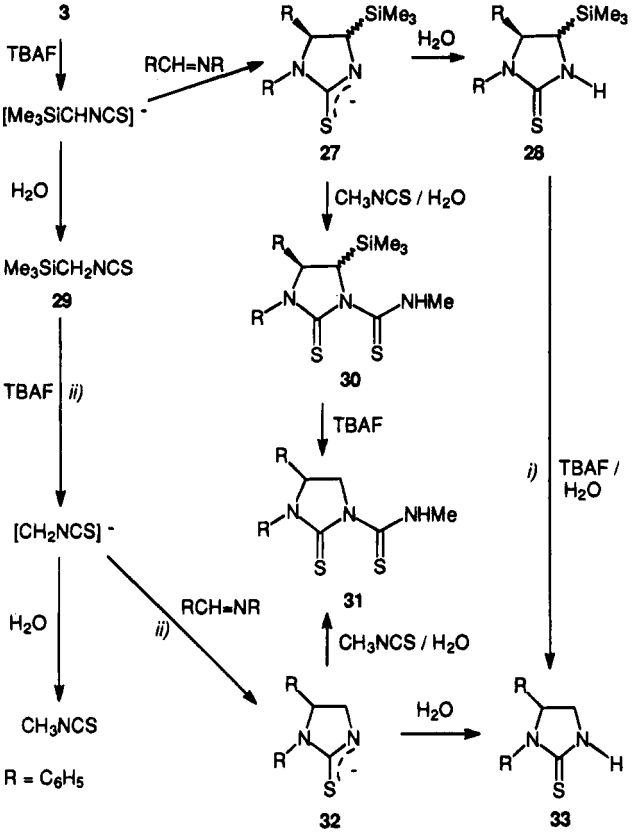
(19) (a) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780−784. (b) Cuevas, J. C.; Patil, P.; Snieckus, V. *Tetrahedron Lett.* **1989**, *30*, 5841−5844. (c) Shimizu, S.; Ogata, M. *J. Org. Chem.* **1987**, *52*, 2314−2315.

(20) It is well known that the 1,2-cycloaddition of isocyanates across the C=O bond of aldehydes and ketones, under thermal or catalytic conditions, affords the corresponding imines. For an exhaustive account on this topic see, for example: Ulrich, H. *Cycloaddition Reactions of Heterocumulenes*; Academic Press: New York, 1967.

Scheme 6



Scheme 7



A 1,3-dipolar cycloaddition was also observed in the TBAF-induced reaction of **2** and **3** with benzylideneaniline. The isocyanate **2** afforded a mixture of the corresponding cycloadducts *cis*- and *trans*-5-phenyl-4-(trimethylsilyl)imidazolidin-2-one (*cis*- and *trans*-**26**, *cis*/*trans* = 1:1.2) (Scheme 6), while the isothiocyanate **3** gave a mixture of 1,5-diphenylimidazolidine-2-thione **33** and of its 3-[methyl(thiocarbamoyl)] derivative **31** (Scheme 7). Our attempts to evidentiate the presence of 5-phenyl-4-(trimethylsilyl)imidazolidin-2-thione **28** in the crude reaction mixture failed. For this reason it is not clear wheter **33** is produced from a desilylation of **28** (step i) or by quenching of the anion **32** with H_2O.[21] This anion is formed by TBAF-induced reaction of the imine with (trimethylsilyl)methyl isothiocyanate (**29**) (step ii). The isothiocyanate **29** is derived from proton abstraction of the anion of **3** from H_2O. The derivative **31** is probably produced from the reaction of the anion **32** with methyl isothiocyanate, which is derived from proton abstraction of $[CH_2NCS]^-$ from H_2O. However, the possibility of an addition of methyl isothiocyanate to the anion **27**, followed by desylilation of the corresponding 3-[methyl(thiocarbamoyl)]-5-phenyl-4-(trimethylsilyl)imidazolidine-2-thione (**30**) cannot necessarily be excluded. The stereostructure of the *cis*- and *trans*-isomers of compounds **23**, **25**, and **26** was assigned from ^1H NMR spectral data. In particular, the C5-H hydrogen of the *cis* resonates downfield with respect to that of the *trans* isomers. The configuration about C4–C5 was further confirmed by means of NOE difference spectra. In fact, a NOE signal enhancement between H4 and H5 was detected only in the *cis*-isomer.

Experimental Section

General. Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Proton and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, in $CDCl_3$ solvent. Chemical shifts are in δ ppm downfield to TMS; signal multiplicities were established by DEPT or APT experiments. Coupling constants J are given in Hz. All reactions were run under a dry nitrogen or argon atmosphere. Bis(trimethylsilyl)methyl azide[22] and [bis(trimethylsilyl)methyl]amine[2a] were prepared according to standard procedures. All the solvents were dried and distilled by standard procedures. The molarity of MeLi, commercially available as *ca.* 1.6 M solution in ethyl ether, was determined according to Lipton.[23]

[[Bis(trimethylsilyl)methyl]imino]triphenylphosphorane (1). Bis(trimethylsilyl)methyl azide (10.00 g, 49.65 mmol) and PPh_3 (13.00 g, 49.56 mmol) in THF (50 mL) were stirred at 25 °C for 2 h. The solvent was removed under reduced pressure, and the crude reaction mixture was treated with *n*-pentane. Filtration gave **1** (18.65 g, 86%). ^1H and ^{31}P NMR spectra of the solid revealed the presence of Ph_3PO as an impurity in 10% amount. ^1H NMR δ −0.09 (s, 18 H), 1.92 (d, 1 H), 7.25–7.72 (m, 15 H); ^{13}C NMR δ −0.3, 35.4, 127.9, 130.5, 132.6, 135.0; ^{31}PNMR ($CDCl_3$, 96 MHZ) δ −0.81; IR (CCl_4) 1437, 1256, 1214 cm^{-1}; MS *m*/*z* 435 (M^+), 420, 362, 263, 183, 172; HRMS (M^+) *m*/*z* calcd for $C_{25}H_{34}NPSi_2$ 435.1967, found 435.1959.

Bis(trimethylsilyl)methyl Isocyanate (2). CO_2 was bubbled into a solution of compound **1** (6.00 g, 13.77 mmol) in ethyl ether (25 mL) at 25 °C for 5 min. The Ph_3PO was filtered, and the solvent was removed. Fractional distillation of the oily residue (63–65 °C, 20 Torr) gave 2.25 g (81%) of **2**.

Reaction of Isocyanate 2 with MeLi Followed by Quenching with H_2O. A solution of the isocyanate **2** (0.11 g, 0.55 mmol) in THF (1.0 mL) was added to a stirred solution of MeLi (0.94 mmol) in THF at 0 °C. The temperature was raised to 25 °C. After 30 min, 1 mL of H_2O was added, and the solution was left to stir for 30 min. After the solvent was

(21) The synthesis of compound **33** directly by TBAF-induced addition of benzylideneaniline to (trimethylsilyl)methyl isothiocyanate (**29**) has been already described. See ref 15.

(22) Palomo, C.; Aizpurua, J.-M.; Garcia, J.-M.; Legido, M. *J. Chem. Soc., Chem. Commun.* **1991**, 524–526.

(23) Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Saphiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155–158.

removed, flash chromatography of the residue (SiO_2, *n*-pentane/EtOAc, 2:1) gave 0.083 g (70%) of **N-[bis(trimethylsilyl)methyl]acetamide (16)**: mp 140–142 °C; ^1H NMR δ −0.04 (s, 18 H), 2.00 (s, 3 H), 3.24 (d, 1 H), 5.18 (d, 1 H); ^{13}C NMR δ −1.4, 23.2, 31.4, 168.9; IR (CCl_4) 3400–3250, 1680 cm^{-1}; MS *m/z* 217 (M^+), 202, 146, 73. Anal. Calcd for $C_9H_{23}NOSi_2$: C, 49.71; H, 10.66; N, 6.44. Found: C, 49.75; H, 10.70; N, 6.41.

Reaction of Isocyanate 2 with Benzaldehyde in the Presence of TBAF. To a cooled solution (−15 °C) of benzaldehyde (0.33 g, 3.11 mmol) and isocyanate **2** (0.62 g, 3.10 mmol) in THF (30 mL) was added TBAF (0.8 mmol) in THF (4 mL), and the reaction mixture was stirred for 15 min. The reaction mixture was diluted with 20 mL of EtOAc, extracted with a 10% aqueous solution of NaCl, and dried over $MgSO_4$. Chromatography (SiO_2, benzene/EtOAc, 2:1) gave 0.10 g (12%) of **benzilidene[bis(trimethylsilyl) methyl]amine (24)** and 0.25 g (34%) of a mixture (1:1) of ***cis*- and *trans*-5-phenyl-4-(trimethylsilyl)oxazolidin-2-one (*cis*- and *trans*-23)**: ^1H NMR δ −0.24 (s, 9 H), 0.07 (s, 9 H), 3.30 (d, 1 H), 3.68 (d, 1 H), 5.37 (d, 1 H), 5.77 (d, 1 H), 6.30–6.50 (b, 1 H), 7.20–7.50 (m, 5 H); ^{13}C NMR relevant resonances δ −3.9, −3.3, 50.7, 51.7, 81.2, 82.1, 161.0, 161.8; IR (CCl_4) 3456, 1750 cm^{-1}; MS *m/z* 235 (M^+), 161. Anal. Calcd for $C_{12}H_{17}NO_2Si$: C, 61.24; H, 7.28; N, 5.95. Found: C, 61.29; H, 7.34; N, 6.00.

Reaction of Isocyanate 2 with Benzylideneaniline in the Presence of TBAF. A solution of isocyanate **2** (0.45 g, 2.24 mmol) in THF (2.0 mL) was added over 3.0 h to a stirred solution of benzylideneaniline (0.53 g, 2.92 mmol) and TBAF (0.6 mmol) in THF (5.0 mL) at −40 °C. A 10% aqueous solution of NH_4Cl (5.0 mL) was added, the temperature was raised to 25 °C, the reaction mixture was diluted with 20 mL of EtOAc, and the organic phase was extracted three times with an aqueous solution of NH_4Cl and dried over $MgSO_4$. *n*-Pentane was then added, and the solid residue was isolated by filtration to give 0.11 g (16%) of *cis*-**26**. The solvent was removed from the solution, and the oily residue was chromatographed (SiO_2, *n*-pentane/EtOAc, 2:1) to give 0.13 g (19%) of *trans*-**26** (*cis*/*trans* = 1:1.2). ***cis*-5-Phenyl-4-(trimethylsilyl)imidazolidin-2-one (*cis*-26)**: mp 235–237 °C; ^1H NMR δ -0.24 (s, 9 H), 3.62 (d, 1 H), 4.90–5.0 (b, 1 H), 5.33 (d, 1 H), 6.90–7.50 (m, 10 H); ^{13}C NMR δ −3.5, 48.5, 64.1, 119.4, 122.7, 127.3, 128.3, 128.5, 128.8, 138.6, 139.2, 161.2; IR (CCl_4) 3450–3200, 1701 cm^{-1}; MS *m/z* 310 (M^+), 73. Anal. Calcd for $C_{18}H_{22}N_2OSi$: C, 69.64; H, 7.14; N, 9.02. Found: C, 69.55; H, 7.20; N, 9.08. ***trans*-5-Phenyl-4-(trimethylsilyl)imidazolidin-2-one (*trans*-26)**: oil; ^1H NMR δ 0.11 (s, 9 H), 3.09 (d, 1 H), 5.09 (d, 1 H), 6.35–6.45 (b, 1 H), 6.90–7.50 (m, 10 H); ^{13}C NMR δ −4.1, 50.3, 64.0, 121.4, 123.8, 126.7, 128.2, 128.5, 128.9, 138.6, 141.0, 161.3; IR (CCl_4) 3450–3200, 1701 cm^{-1}; MS *m/z* 310 (M^+), 73. Anal. Calcd for $C_{18}H_{22}N_2OSi$: C, 69.64; H, 7.14; N, 9.02. Found: C, 69.58; H, 7.08; N, 9.06.

Bis(trimethylsilyl)methyl Isothiocyanate (3). Compound **1** (0.77 g, 1.77 mmol) and CS_2 (4 mL) were refluxed in toluene (15 mL) for 4 h. The solvent was removed under vacuum, and the crude reaction mixture was chromatographed (SiO_2, *n*-pentane) to yield 0.32 g (83%) of isothiocyanate **3**.

Reaction of Isothiocyanate 3 with Benzylideneaniline in the Presence of TBAF. A solution of isothiocyanate **3** (0.30 g, 1.38 mmol) in THF (2.0 mL) was added over 3.0 h to a stirred solution of benzylideneaniline (0.38 g, 2.10 mmol) and TBAF (0.4 mmol) in THF (5.0 mL) at −78 °C. A 10% aqueous solution of NH_4Cl (5.0 mL) was added at −70 °C. After the temperature was raised to 25 °C, the reaction mixture was diluted with 20 mL of EtOAc, and the organic phase was extracted three times with an aqueous solution of NH_4Cl and dried over $MgSO_4$. *n*-Pentane was then added, and the solid residue was isolated by filtration to give 0.08 g (22%) of 1,5-diphenylimidazolidine-2-thione (**33**). The solvent was removed from the solution, and the residue was chromatographed (SiO_2, n-pentane/EtOAc, 2:1) to give 0.08 g (18%) of derivative **31**. **1,5-Diphenylimidazolidine-2-thione (33)**: mp 188–190 °C (lit.[15] mp 188–190 °C). **3-[Methyl(thiocarbamoyl)]-1,5-diphenylimidazolidine-2-thione (31)**: oil; ^1H NMR δ 3.21 (d, 3 H), 4.62 (m, 1 H), 5.00–5.15 (m, 2 H), 6.60–7.30 (m, 10 H), 12.2–12.4 (m, 1 H); ^{13}C NMR relevant resonances δ 32.3, 58.0, 63.5, 137.8, 137.9 177.8, 180.9; IR (CCl_4) 3450–3200, 1556, 1500, 1470, 1420, 1390, 1280, 1220, 1100, 1070 cm^{-1}; MS *m/z* 327 (M^+), 254, 181, 77, 73. Anal. Calcd for $C_{17}H_{17}N_3S_2$: C, 62.35; H, 5.23; N, 12.83. Found: C, 62.29; H, 5.28; N, 12.86.

N,N'-[Bis(trimethylsilyl)methyl]carbodiimide (4). Compound **1** (0.85 g, 1.95 mmol) and isocyanate **2** (0.39 g, 1.94 mmol) were reacted in refluxing benzene (25 mL) for 1 h. The solvent was removed under vacuum, and the crude reaction mixture was treated with 50 mL of *n*-pentane. After the PPh_3O was filtered and the solvent evaporated, flash chromatography (SiO_2, *n*-pentane/Et_2O, 14:1) gave 0.53 g (76%) of carbodiimide **4**: oil; ^1H NMR δ 0.07 (s, 36 H), 2.13 (s, 2 H); ^{13}C NMR δ −1.1, 39.4, 139.2; IR (CCl_4) 2103, 1262 cm^{-1}; MS *m/z* 285 (M^+ − 73), 173, 172, 73. Anal. Calcd for $C_{15}H_{38}N_2Si_4$: C, 50.21; H, 10.67; N, 7.81. Found: C, 50.19; H, 10.73; N, 7.76.

***N*-Phenyl-*N'*-[Bis(trimethylsilyl)methyl]carbodiimide (5). A.** *N*-Phenyltriphenylphosphinimine (1.43 g, 4.04 mmol) and isocyanate **2** (0.80 g, 4.00 mmol) were refluxed in benzene for 3 h. The solvent was removed under vacuum, and the crude reaction mixture was treated with 50 mL of *n*-pentane. After the Ph_3PO was filtered and the solvent evaporated, flash chromatography (SiO_2, *n*-pentane/Et_2O, 14:1) gave 0.91 g (82%) of carbodiimide **5**: oil; ^1H NMR δ 0.17 (s, 18 H), 2.43 (s, 1 H), 7.00–7.32 (m, 5 H); ^{13}C NMR δ −1.3, 39.5, 123.2, 123.8, 129.3, 131.0, 142.4; IR (CCl_4) 2133, 1595, 1500 cm^{-1}; MS *m/z* 276 (M^+), 261, 172, 73. Anal. Calcd for $C_{14}H_{24}N_2Si_2$: C, 60.81; H, 8.75; N, 10.13. Found: C, 60.86; H, 8.70; N, 10.17.

B. Compound **1** (0.75 g, 1.72 mmol) and phenyl isocyanate (0.20 g, 1.72 mmol) were refluxed in benzene (10 mL) for 2 h. An ^1H NMR spectrum of the reaction mixture and a GC analysis revealed the presence of a mixture of **2**, **5**, and **6** (**5**/**6** = 2.5). Flash chromatography (SiO_2, *n*-pentane/Et_2O, 14:1) gave 0.27 g (56%) of **5**.

Reaction of *N*-Phenyl-*N'*-[bis(trimethylsilyl)methyl]-carbodiimide (5) with CF_3COOH. CF_3COOH (0.05 g, 0.40 mmol) was added to a $CDCl_3$ solution (1.00 mL) of **5** (0.11 g, 0.40 mmol) at 25 °C. The solvent was removed under vacuum, and the oily residue was extracted with *n*-pentane to give 0.13 g (83%) of **1-(bis(trimethylsilyl)methyl]-3-phenyl-2-(trifluoroacetyl)isourea (7)**: oil; ^1H NMR δ 0.11 (s, 18 H), 3.08 (d, 1 H), 7.20–7.50 (m, 5 H), 8.44 (d, 1 H); ^{13}C NMR relevant resonances δ −1.4, 33.6, 129.0, 129.6, 134.6, 153.1; IR (CCl_4) 3500–3100, 1786, 1730, 1549 cm^{-1}; MS *m/z* 390 (M^+), 375. Anal. Calcd for $C_{16}H_{25}F_3N_2O_2Si_2$: C, 49.21; H, 6.45; N, 7.17. Found: C, 49.19; H, 6.49; N, 7.14.

Reaction of *N*-Phenyl-*N'*-[bis(trimethylsilyl)methyl]-carbodiimide (5) with MeLi Followed by Addition of H_2O. A 1.5 M solution of MeLi in ethyl ether (4.0 mL, 6.00 mmol) was added to a stirred solution of **5** (0.28 g, 1.01 mmol) in THF (3.0 mL) at 0 °C. After 30 min H_2O (1 mL) was added. The solution was left at 25 °C for 30 min and then extracted with an acqueous solution of NH_4Cl. The solvent was removed under vacuum and chromatographed (SiO_2, *n*-pentane/EtOAc, 1:1) to give 0.25 g (85%) of **[bis(trimethylsilyl)methyl)[1-(phenylimino)ethyl]amine (17)**: oil; ^1H NMR ($CDCl_3$) δ 0.09 (s, 18 H), 1.77 (s, 3 H), 3.55 (d, 1 H), 3.90 (d, 1 H), 6.80–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −1.2, 17.9, 31.5, 121.3, 122.2, 128.6, 134.1, 154.4; IR (CCl_4) 1620 cm^{-1}; MS *m/z* 292 (M^+), 277, 118. Anal. Calcd for $C_{15}H_{28}N_2Si_2$: C, 61.58; H, 9.65; N, 9.57. Found: C, 61.57; H, 9.71; N, 9.53.

In another experiment, MeLi (0.40 mmol) was added to a stirred solution of **5** (0.06 g, 0.21 mmol) in THF (3.0 mL) at −40 °C. After 30 min, H_2O (0.2 mL) was added. The solvent was removed under vacuum at −40 °C, and the residue was dissolved in 1.0 mL of $CDCl_3$ and then transferred in a ^1H NMR tube. The ^1H NMR spectrum recorded at −40 °C revealed the presence of compound **17** as the single regioisomer.

Reaction of *N*-Phenyl-*N'*-[bis(trimethylsilyl)methyl]-carbodiimide (5) with MeLi Followed by Addition of MeI. A 1.5 M solution of MeLi in ethyl ether (4.0 mL, 6.00 mmol) was added to a stirred solution of **5** (0.28 g, 1.00 mmol) in THF (3.0 mL) at 0°C. After 30 min 0.90 g (6.34 mmol) of

MeI was added. The solution was left to stand at 25 °C for 30 min and then extracted with an aqueous solution of NH_4Cl. The solvent was removed under vacuum and chromatographed (SiO_2, *n*-pentane/EtOAc, 1:1) to give 0.20 g (65%) of **[1-[[bis(trimethylsilyl)methyl]imino]ethyl]methylphenylamine (18)**: oil; ^1H NMR δ 0.05 (s, 18 H), 1.67 (s, 3 H), 2.64 (s, 1 H), 3.14 (s, 3 H), 6.95–7.40 (m, 5H); ^{13}C NMR δ −1.2, 14.9, 39.8, 44.8, 124.0, 125.8, 128.9, 138.7, 153.2; IR (CCl_4) 1622, 1594, 1495 cm^{-1}; MS *m/z* 306 (M^+), 291, 233, 73. Anal. Calcd for $C_{16}H_{30}N_2Si_2$: C, 62.68; H, 9.86; N, 9.14. Found: C, 62.65; H, 9.82; N, 9.16.

Compound **18** (0.04 g, 0.13 mmol) and CF_3COOH (0.01 g, 0.13 mmol) in 0.7 mL of $CDCl_3$ gave the corresponding **[1-[[bis(trimethylsilyl)methyl]imino]ethyl]methylphenylamine trifluoroacetate (19)**: oil; ^1H NMR δ 0.10 (s, 18 H), 2.00–2.15 (b, 3H), 2.74 (d, 1 H), 3.54 (s, 3 H), 7.00–7.40 (m, 5 H), 8.10–8.40 (bd, 1 H).

Diphenylketene *N*-[Bis(trimethylsilyl)methyl]imine (9a). Compound **1** (2.00 g, 4.59 mmol) and diphenylketene (0.89 g, 4.59 mmol) were stirred in Et_2O (25 mL) for 1 h at 25 °C. The solvent was removed under vacuum, and the crude reaction mixture was treated with 50 mL of *n*-pentane and left at 0 °C for 15 h. After a solid residue was filtered, the evaporation of the solvent afforded 1.14 g (71%) of the ketene imine **9a** still contaminated by amounts (<10%) of **1** and of Ph_3P: oil; ^1H NMR δ 0.10 (s, 18 H), 2.91 (s, 1 H), 7.20–7.40 (m, 10 H); ^{13}C NMR δ −1.1, 48.4, 73.0, 125.4, 127.1, 128.5, 136.2, 180.7; IR (CCl_4) 1993 cm^{-1}; MS *m/z* 351 (M^+), 278, 166; HRMS (M^+) *m/z* calcd for $C_{21}H_{29}NSi_2$ 351.1839, found 351.1848.

(Trimethylsilyl)ketene *N*-[Bis(trimethylsilyl)methyl]imine (9b). A solution of (trimethylsilyl)ketene (1.60 g, 14.03 mmol) in 10.0 mL of Et_2O was slowly added (7 h) to a stirred solution of **1** (3.80 g, 8.72 mmol) in Et_2O (10.0 mL) at 25 °C. After the removal of the solvent, the amount of **9b** in the crude reaction mixture was determined by IR (4.90 mmol, 56%). The oily residue was distilled under vacuum (57–59 °C, 0.01 Torr) to give 1.00 g (42%) of **9b**: oil; ^1H NMR δ 0.09 (s, 18 H), 0.10 (s, 9 H), 2.44 (d, 1 H), 2.62 (d, 1 H); ^{13}C NMR δ −1.0, 0.5, 31.7, 45.6, 176.6; IR (CH_2Cl_2, ϵ = 116.0) 2010 cm^{-1}; MS *m/z* 271 (M^+), 256, 198, 73. Anal. Calcd for $C_{12}H_{29}NSi_3$: C, 53.06; H, 10.76; N, 5.16. Found: C, 53.01; H, 10.82; N, 5.18.

Dimethylketene *N*-[Bis(trimethylsilyl)methyl]imine (10). Compound **2** (1.73 g, 8.58 mmol) was added to salt-free isopropylidenetriphenylphosphorane (2.61 g, 8.58 mmol) in toluene (50 mL) and the resulting mixture stirred for 2 h at 25 °C. After the removal of the solvent, the crude reaction mixture was distilled (10^{-2} Torr, 120 °C) in a short-path Kugelrohr apparatus to give 0.80 g (41%) of ketene imine **10**: oil; ^1H NMR δ 0.06 (s, 18 H), 1.59 (s, 6 H) 2.45 (s, 1 H); ^{13}C NMR δ −1.4, 16.5, 49.2, 54.0, 184.8; IR (CCl_4) 2011 cm^{-1}; MS *m/z* 227 (M^+), 212, 154, 73; HRMS (M^+) *m/z* calcd for $C_{11}H_{25}NSi_2$ 227.1526, found 227.1520.

***N*-[Bis(trimethylsilyl)methyl]propionamide (11).** A solution of propionyl chloride (1.26 g, 13.60 mmol) in 2.0 mL of Et_2O was added to a stirred solution of *N*-[bis(trimethylsilyl)methyl]amine (2.39 g, 13.60 mmol) and collidine (2.38 g, 19.70 mmol) in Et_2O (60.0 mL) at 0 °C. After the collidine chloride was filtered and the solvent evaporated, flash chromatography (SiO_2, CH_2Cl_2) gave 2.14 g (68.0%) of amide **11**: oil; ^1H NMR δ 0.04 (s, 18 H), 1.16 (t, 3 H), 2.22 (q, 2 H), 3.23 (d, 1 H), 5.10–5.30 (bd, 1 H); ^{13}C NMR δ 1.4, 10.7, 29.9, 31.3, 172.8; IR (CCl_4) 3400–3200, 1671 cm^{-1}; MS *m/z* 231 (M^+), 217, 174. Anal. Calcd for $C_{10}H_{25}NOSi_2$: C, 51.89; H, 10.89; N, 6.05. Found: C, 51.85; H, 10.83; N, 6.09.

Attempted Synthesis of Methylketene *N*-[Bis(trimethylsilyl)methyl]imine (12). To a stirred solution of PPh_3 (9.17 g, 35.00 mmol) in CH_2Cl_2 (35.0 mL) was added at −10 °C a solution of bromine (5.60 g, 35.00 mmol) in CH_2Cl_2 (10 mL). Et_3N (10.0 mL) and the amide **11** (2.31 g, 10.00 mmol) were added under an argon atmosphere. After 4 h, the IR analysis of the crude reaction mixture revealed the disappearance of the signal of the C=O of the amide at 1671 ($\nu_{NC=O}$), while the resonance at 2010 cm^{-1} ($\nu_{C=C=N}$), which could be attributed to the ketene imine **11**, reached its maximum. The solvent was evaporated under vacuum at −10 °C and the residue was treated with 50 mL of *n*-pentane and cooled at −20 °C for 1 h. After filtration of the precipitate under an argon atmosphere, our attempts to purify the ketene imine in the remaining solution were frustrated; only compounds **11** and **13** were isolated. In another identical experiment, 5 mL of H_2O was added to a reaction mixture as soon as the amount of ketene imine reached its maximum and the amide **11** totally disappeared. The organic layer was dried over $MgSO_4$. After evaporation of the solvent, the crude residue was chromatographed (SiO_2, *n*-pentane/EtOAc, 3:1) to give 0.37 g (16%) of **11** and 1.52 g (4.90 mmol, 49%) of **13**. ***N*-bis(trimethylsilyl)methyl]-2-bromopropionamide (13)**: mp 151–153 °C; ^1H NMR δ 0.07 (s, 9 H), 0.08 (s, 9 H), 1.88 (d, 3 H), 3.14 (d, 1 H), 4.47 (q, 1 H), 6.20–6.30 (b, 1 H); ^{13}C NMR δ 1.5, 23.9, 32.1, 46.5, 168.0; IR (CCl_4) 3400–3200, 1660, 1253 cm^{-1}; MS *m/z* 295 (M^+-Me), 237, 174, 73. Anal. Calcd for $C_{10}H_{24}BrNOSi_2$: C, 38.70; H, 7.79; N, 4.51. Found: C, 38.66; H, 7.84; N, 4.47.

Reaction of Ketene Imines 9a and 9b with MeLi Followed by Quenching with MeI and Me_2CHI. General Procedure. A solution of the ketene imines **9a** and **9b** in THF was added to a stirred solution of MeLi (1.12 mmol) in THF at 25 °C. After 2 h, the selected iodide was added. The solvent was removed, and the residue was treated with *n*-pentane and cooled at −20 °C for 2 h. The clear solution was removed, and filtered, and the solvent was evaporated. This workup was performed twice. An oily residue containing the ketene imines **20–22** was obtained. The analytical purities of **20–22** were determined by adding an exact amount of CH_2Cl_2, as the internal standard, to a solution of **20–22** in $CDCl_3$. The relative amounts of **20–22** with respect to CH_2Cl_2 were determined by integration of the ^1H NMR resonances at 1.44 ppm (**20**), 1.55 (**21**), and 1.09 (**22**) with respect to the resonance of CH_2Cl_2 at 5.32 ppm.

Reaction of Diphenylketene *N*-[1,1-Bis(trimethylsilyl)methyl]imine 9a with MeLi Followed by Quenching with MeI. The ketene imine **9a** (0.22 g, 0.62 mmol), MeLi (1.12 mmol), and MeI (0.07 mL, 1.12 mmol) in THF (5.0 mL) gave 0.19 g of an oily residue containing the **diphenylketene N-[1,1-bis(trimethyl)silyl)ethyl]imine (20)** (0.14 g, 66%): oil; ^1H NMR δ 0.08 (s, 18 H), 1.44 (s, 3 H), 7.20–7.40 (m, 10 H); ^{13}C NMR δ −1.2 , 19.5, 48.0, 76.6, 125.4, 127.5, 128.2, 136.0, 180.0; IR (CCl_4) 1993, 1252 cm^{-1}; MS *m/z* 365 (M^+), 350; HRMS (M^+) *m/z* calcd for $C_{22}H_{31}NSi_2$ 365.1995, found 365.1999.

Reaction of (Trimethylsilyl)ketene *N*-[Bis(trimethylsilyl)methyl]imine (9b) with MeLi Followed by Quenching with MeI and with Me_2CHI. (A). The ketene imine **9b** (0.10 g, 0.37 mmol), MeLi (0.74 mmol), and MeI (0.05 mL, 0.74 mmol) in THF (5 mL) gave 0.09 g of an oily residue containing the **(trimethylsilyl)ketene N-[1,1-bis(trimethylsilyl)ethyl]imine (21)** (0.07 g, 65%): oil; ^1H NMR δ 0.06–0.07 (b, 27 H), 1.55 (s, 3 H), 2.44 (s, 1 H); ^{13}C NMR δ −1.1, 11.0, 41.7, 46.5, 176.1; IR (CCl_4) 1996, 1251 cm^{-1}; MS *m/z* 285 (M^+), 270, 212, 172; HRMS (M^+) *m/z* calcd for $C_{13}H_{31}NSi_3$ 285.1764, found 285.1756.

(B). The ketene imine **9b** (0.10 g, 0.37 mmol), MeLi (0.74 mmol), and Me_2CHI (0.05 mL, 0.74 mmol) in THF (5 mL) gave 0.10 g of an oily residue containing the **(trimethylsilyl)ketene N-[2-methyl-1,1-bis(trimethylsilyl)propyl]imine (22)** (0.06 g, 54%): oil; ^1H NMR δ 0.11 (s, 18 H), 0.12 (s, 9 H), 1.09 (d, 6 H), 2.11 (m, 1 H), 2.52 (s, 1 H); ^{13}C NMR δ −0.7, 0.18, 25.1, 27.5, 46.4, 55.7, 179.7; IR (CCl_4) 1994, 1248 cm^{-1}; MS *m/z* 313 (M^+), 298, 270, 240; HRMS (M^+) *m/z* calcd for $C_{15}H_{35}NSi_3$ 313.2077, found 313.2082.

Reaction of Diphenylketene *N*-[1,1-Bis(trimethylsilyl)methyl]imine (9a) with Benzaldehyde in the Presence of TBAF. The ketene imine **9a** (0.30 g, 0.86 mmol) in THF (5.0 mL) was added at −15 °C to a cooled (−15 °C) solution of benzaldehyde (0.16 g, 1.54 mmol) and TBAF (0.26 mmol) in THF (6.0 mL). The temperature was raised to −5 °C, and the reaction mixture was stirred for 45 min. The reaction mixture was diluted with 20 mL of EtOAc, extracted with 10% aqueous NaCl, and dried over $MgSO_4$. Removal of the solvent afforded 0.28 g of an oily residue containing 0.18 g (54%) of *cis*- and *trans*-**25** (*cis*/*trans* = 1:2). The amount and the isomeric distribution of compounds *cis*- and *trans*-**25** were determined by adding an exact amount of CH_2Cl_2 to a solution in $CDCl_3$

of the crude reaction mixture and by calculating the relative amounts of *cis*- and *trans*-**25** with respect to CH_2Cl_2 by integration of the ^1H NMR resonances at 0.03, 3.5, 5.26, 5.35 ppm (*trans*-**25**) and at −0.31, 3.89, 5.30, 5.85 ppm (*cis*-**25**) with respect to the resonance of CH_2Cl_2 at 5.32 ppm. Chromatography (SiO_2, *n*-pentane/EtOAc, 2:1) afforded 0.12 g of a 1:2 *cis*/*trans* mixture of *cis*- and *trans*-**25** (37%). ***cis*- and *trans*-2-benzhydryl-4-(trimethylsilyl)-5-phenyl-1,3-oxazoline (*cis*- and *trans*-25)**: oil; ^1H NMR δ −0.31 (s, 9 H), 0.03 (s, 9 H), 3.50 (d, 1 H), 3.89 (d, 1H), 5.26 (s, 1 H), 5.30 (s, 1 H), 5.35 (d, 1 H), 5.85 (d, 1 H), 6.90−7.50 (m, 15 H); ^{13}C NMR relevant resonances ($CDCl_3$) δ −3.8, −2.3, 51.2, 51.5, 64.2, 66.4, 83.5, 84.8, 164.4, 165.4; IR (CCl_4) 1653, 1495, 1448, 1251 cm^{-1}; MS *m*/*z* 385 (M^+), 312, 167. Anal. Calcd for $C_{25}H_{27}NOSi$: C, 77.88; H, 7.06; N, 3.63. Found: C, 77.83; H, 7.01; N, 3.67.

[Bis(trimethylsilyl)methyl]sulfinylamine (14). Bis-[(trimethylsilyl)methyl]amine (1.00 g, 5.70 mmol), thionyl chloride (0.71 g, 6.00 mmol), and Et_3N (1.21 g, 12.00 mmol) were stirred in ethyl ether (15 mL) for 30 min at −30 °C then at 10 °C for 10 min. The $Et_3NH^+Cl^-$ was filtered, and the solvent was removed under vacuum. The oily residue was distilled at 86 °C (15.0 Torr) to give 0.82 g (65%) of **14**: oil; ^1H NMR δ −0.12 (s, 18 H), 4.71 (s, 1 H); ^{13}C NMR δ −1.5, 53.4; IR (CCl_4) 1252, 1210, 1063 cm^{-1}; MS *m*/*z* 221 (M^+), 173, 172, 148, 147. Anal. Calcd for $C_7H_{19}NSOSi_2$: C, 37.96; H, 8.65; N, 6.32. Found: C, 38.00; H, 8.60; N, 6.27. Compound **14** (0.11 g, 0.5 mmol) and trimethyloxonium tetrafluoroborate (0.07 g, 0.5 mmol) in 2.0 mL of CH_3NO_2 gave the corresponding **N-[1,1-bis(trimethylsilyl)methyl]methylsulfinylimmonium tetrafluoroborate (15)**: oil; ^1H NMR ($CDCl_3$) δ −0.12 (s, 18 H), 2.18 (b, 1 H), 6.30−5.80 (b, 3 H).

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Supporting Information Available: Listing of ^1H and ^{13}CNMR data, accompanied by subjective peak assignments (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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