hydroporphyrins due to serious loss of compound by oxidation. Loss was substantial, even at room temperature. In contrast to the results reported for exchange reactions of zinc tetraphenylhydroporphyrins in *tert*-butoxide/*tert*-butyl alcohol-d_1 mixtures,[36] no evidence was seen for deuterium incorporation in the β-pyrroline protons. Macrocycles recovered from hydroporphyrin oxidation in this medium and in D_2SO_4 were deuteriated at meso positions to a greater extent than expected for that compound, suggesting that exchange of meso protons in cation radicals or related intermediates is rapid.

Mechanistic Considerations. The mechanism of acid-catalyzed deuterium exchange in tetrapyrrolic macrocycles is not understood. In strong acid media, compounds are present at at least three levels of protonation: $H_2(P)$, $H_3(P)^+$, and $H_4(P)^{2+}$. The thermodynamically preferred sites of protonation are the central nitrogen atoms. Numerous carbon-protonated tautomers can be written, however. Tautomers of these and perhaps other levels of protonation must be important in the reaction mechanism of this electrophilic substitution reaction. The level of protonation and the identity of the tautomers that are directly involved as intermediates or activated compounds in deuterium exchange have not been established. It has been suggested that it is the neutral porphyrin that undergoes electrophilic attack.[4] This proposal was based upon the slower rates of deuterium exchange in the strong acid TFA-d_1 compared to exchange in the weaker acid acetic acid-d_1. Other have argued that comparisons of the rapid rate of deuterium exchange in D_2SO_4 with estimates of the proportion of neutral porphyrin present and reasonable encounter rates make it unlikely that neutral porphyrin is involved in the reaction.[2]

The results presented in this paper are not consistent with a single mechanism of exchange for all tetrapyrrole compounds in all acidic reaction media. We have demonstrated that the gross specificity of exchange within an individual compound is similar in TFA and D_2SO_4. However, changing the reaction medium from the former to the latter greatly accelerates the exchange rate of H_2(OEP) but decreases or has little effect on the exchange rates of oxoporphyrin and hydroporphyrin compounds. This result establishes that oxoporphyrin and hydroporphyrin compounds must react by different mechanisms than that of the porphyrin. Furthermore, it is now clear that the rate of deuterium exchange does not increase monotonically with the acid strength of the reaction medium for any of these tetrapyrrole systems. We have demonstrated that the selectivity of deuteriation catalyzed by *p*-toluenesulfonic acid-d_1 is different in *o*-dichlorobenzene solution than in the melt. These observations imply that specific interactions of the tetrapyrrole, the acid or its conjugate base, and the solvent are extremely important in these reactions. Support for this conclusion is provided by the report of strong association between H_4(OEP)$^{2+}$ and its counteranions.[37]

Acknowledgment. We gratefully acknowledge the Camille and Henry Dreyfus Foundation (A.M.S.), the Research Corporation, the NIH (Grants GM33882 and BRSG S07 RR07044), and the Brandeis Undergraduate Research Program (M.A.L.) for support of this research. We thank Dr. Harold Goff for providing a preprint of ref 11.

(36) Whitlock, H. W.; Oester, M. Y. *J. Am. Chem. Soc.* **1973**, *95*, 5738.

(37) Ogoshi, H.; Watanabe, E.; Yoshida, Z. *Tetrahedron* **1973**, *29*, 3241.

Silyl-Substituted Thioimidates as Nitrile Ylide Equivalents

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Received August 20, 1986

Treatment of silyl-substituted thioimidates with silver fluoride in the presence of a trapping agent produces dipolar cycloadducts formally derived from nitrile ylides. The ratio of cycloadducts obtained from the reaction of unsymmetrically substituted dipolarophiles with phenyl silyl thioimidate 8 was found to be significantly different from that obtained from the photolysis of phenylazirine. We propose that the different product ratios encountered with silyl thioimidate 8 result from the operation of a mechanism which does not proceed via a nitrile ylide dipole. Generation of an intermediate having azomethine ylide reactivity can be achieved by silver ion complexation with the silyl thioimidate. Desilylation of the resulting complex with fluoride ion generates an azomethine ylide which undergoes 1,3-dipolar cycloaddition with added dipolarophiles. The resulting cycloadduct loses methyl mercaptan to give products which are equivalent to those obtained from nitrile ylides.

1,3-Dipoles can be classified into two major types: (1) those with internal octet stabilization, where a mesomeric formula can be drawn such that the central atom of the dipole has a positive charge and all centers have completely filled valences, and (2) those without internal octet stabilization, where each mesomeric form has an electron sextet.[1,2] By far the more common group of dipoles is the former, mainly because the dipoles in the second group are all unstable and must be prepared in situ. In recent years our interest has focused on the chemistry of the octet-stabilized class of dipoles known as the nitrile ylides.[3-6] 1,3-Dipolar cycloaddition of this class of dipoles has been

(1) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1973**, *2*, 565, 633.
(2) Huisgen, R. *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984; Vol. 1, Chapter 1.

(3) Padwa, A. *Acc. Chem. Res.* **1976**, *9*, 371.
(4) Padwa, A.; Carlsen, P. H. J. *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1982; Vol. 2, p 55.
(5) Padwa, A.; Clough, S.; Dharan, M.; Smolanoff, J.; Wetmore, S. I. *J. Am. Chem. Soc.* **1972**, *94*, 1395; **1973**, *95*, 1945, 1954; *J. Org. Chem.* **1973**, *38*, 1333.
(6) Padwa, A.; Carlsen, P. H. J. *J. Am. Chem. Soc.* **1975**, *97*, 3862; **1976**, *98*, 2006; **1977**, *99*, 1514.

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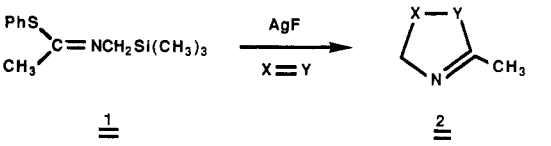
widely investigated and in many cases has led to the synthesis of a variety of interesting heterocyclic compounds, some of which would be tedious to synthesize by other routes.[7,8] Probably the most general synthetic approach to nitrile ylides involves the photolysis of aryl-substituted azirines.[3,7,9] A long-standing restriction to the further use of nitrile ylides in organic synthesis stems from the fact that simple alkyl-substituted systems are not easily prepared. In searching for alternate ways to form these dipoles, we have studied the desilylation of several silyl thioimidates as a potential route for nitrile ylide formation.[16] We report here the results of these studies.

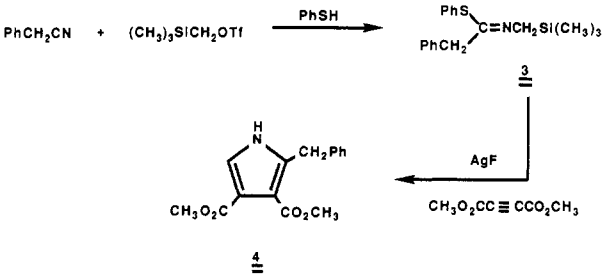
Results and Discussion

The desilylation of α-trimethyl onium salts by fluoride ion has been widely utilized in recent years as a convenient method for preparing nitrogen and sulfur ylides.[17-30] By far the most extensively studied application of the desilylation method is in the generation of azomethine ylides.[17,22-26] Relatively little work has been done, however, using the trimethylsilyl functionality as a leaving group for the generation of nitrile ylides.[30] In an earlier publication we reported that exposure of methyl silyl thioimidate 1 to silver fluoride in the presence of a variety of dipolarophiles resulted in the formation of 1,3-dipolar cycloadducts.[16] The isolation of structures of type 2 was



1 2

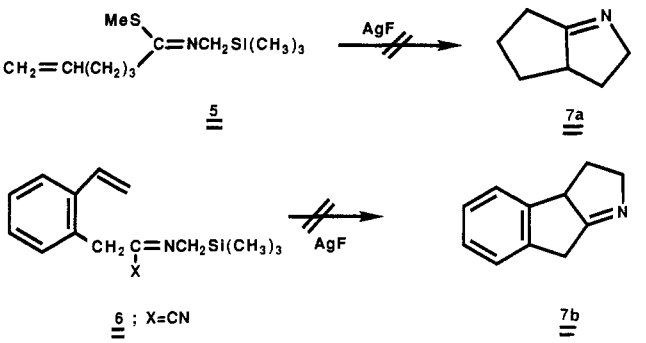
consistent with the involvement of a nitrile ylide intermediate. This result prompted us to examine the reaction of other silyl thioimidates with silver fluoride. We found that benzyl silyl thioimidate 3 proceeded in an analogous fashion to that encountered with 1, giving rise to pyrrole 4 in 74% yield when treated with silver fluoride in the



3 4

presence of DMAD. Silyl thioimidate 3 was conveniently prepared by heating equimolar quantities of phenylacetonitrile and (trimethylsilyl)methyl triflate at 80 °C for 25 min followed by the addition of thiophenol.

Intramolecular dipolar cycloadditions have much synthetic potential.[31,32] To apply the above methodology in this context, we investigated the silver fluoride induced reaction of silyl thioimidates 5 and 6. We found, however,



5 7a

6 ; X=CN 7b

that no signs of an internal cycloadduct could be detected in the crude reaction mixture. This result was somewhat surprising since nitrile ylides generated from the photolysis of azirines are known to undergo intramolecular cycloaddition to unactivated π-bonds.[33] Thus, it would appear as though the reactive intermediate generated from the desilylation reaction is behaving differently from that derived from the azirine photolysis. It therefore became of interest to compare the features of nitrile ylide cycloaddition of an azirine with those of cycloaddition by the "desilylation procedure". This led us to synthesize phenyl silyl thioimidate 8 as a potential precursor of nitrile ylide 9. Phenylazirine (10) is readily available and had previously been demonstrated to produce nitrile ylide 9 on irradiation.[5]

Phenyl silyl thioimidate 8 could not be prepared by the same method previously employed for the synthesis of 1 and 3. Reaction of benzonitrile with (trimethylsilyl)methyl triflate failed to give an intermediate nitrilium salt. The conjugative nature of the phenyl ring decreases the nu-

(7) Gilgen, P.; Heimgartner, H.; Schmid, H.; Hansen, H. J. *Heterocycles* **1977**, *6*, 143.

(8) Hansen, H. J.; Heimgartner, H. *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience, New York, 1984; Vol. 1, Chapter 2.

(9) Alternate approaches to nitrile ylides involve (a) treatment of imidoyl halides with base,[10] thermal or photochemical elimination of phosphoric acid esters from 4,5-dihydro-1,3,5-oxazaphospholes,[11] and photolysis of carbene precursors in nitrile solvents.[12-15]

(10) Huisgen, R.; Stangle, H.; Sturm, H. J.; Wagenhofer, H. *Angew Chem.* **1962**, *74*, 31.

(11) Burger, K.; Fehn, J. *Chem. Ber.* **1972**, *105*, 3814.

(12) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc.* **1982**, *104*, 6813.

(13) Kende, A. S.; Hebeisen, P.; San Filippo, P. J.; Toder, B. H. *J. Am. Chem. Soc.* **1982**, *104*, 4244.

(14) Barcus, R. L.; Wright, B. B.; Platz, M. S.; Scaiano, J. C. *Tetrahedron Lett.* **1983**, *24*, 3955.

(15) Grasse, P. B.; Brauer, B. E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833.

(16) For some earlier work in this area, see: (a) Turro, N. J.; Cha, Y. C.; Gould, I. R.; Padwa, A.; Gasdaska, J. R.; Tomas, M. *J. Org. Chem.* **1985**, *50*, 4415; (b) *J. Am. Chem. Soc.* **1986**, *108*, 6739. In our earlier communication,[16a] we had assumed that treatment of silyl thioimidates with silver fluoride generated nitrile ylides as 1,3-dipoles. However, additional work (see ref 34[16b]) suggested the possible involvement of a silver complexed (or protonated) azomethine ylide intermediate as outlined in Scheme II.

(17) Vedejs, E.; Martinez, G. R. *J. Am. Chem. Soc.* **1979**, *101*, 6452.

(18) Cohen, T.; Kosarych, Z.; Suzuki, K.; Yu, L. C. *J. Org. Chem.* **1985**, *50*, 2965.

(19) Schmidbauer, H. *Acc. Chem. Res.* **1975**, *8*, 62.

(20) Kocienski, P. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1096.

(21) Cooke, F.; Magnus, P.; Bundy, G. L. *J. Chem. Soc., Chem. Commun.* **1978**, 714.

(22) Smith, R.; Livinghouse, T. *J. Org. Chem.* **1983**, *48*, 1554.

(23) Vedejs, E.; West, F. G. *J. Org. Chem.* **1983**, *48*, 4773.

(24) Tsuge, O.; Kanemasa, S.; Matsuda, K. *Chem. Lett.* **1985**, 1411.

(25) Achiwa, K.; Sekiya, M. *Heterocycles* **1983**, *20*, 167.

(26) Padwa, A.; Haffmanns, G.; Tomas, M. *J. Org. Chem.* **1984**, *49*, 3314.

(27) Gassman, P. G.; Miura, T. *Tetrahedron Lett.* **1981**, *22*, 4787.

(28) Sato, Y.; Sakakirbara, H. J. *J. Organomet. Chem.* **1979**, *166*, 303. Sato, Y.; Yagi, Y.; Koto, M. J. *J. Org. Chem.* **1980**, 45, 613.

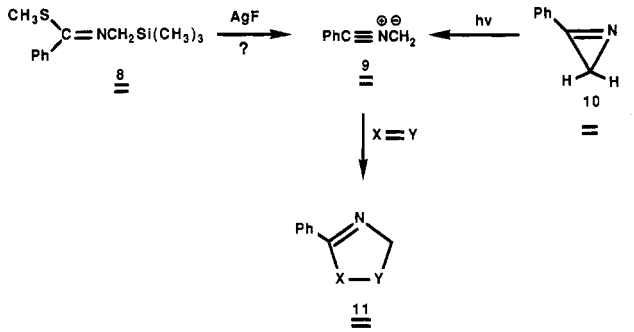
(29) Fleischmann, C.; Zbiral, E. *Tetrahedron* **1978**, *34*, 317.

(30) Tsuge, O.; Kanemasa, S.; Matsuda, K. *Chem. Lett.* **1985**, 1411; **1984**, 801. Tsuge, O.; Kanemasa, S.; Yamada, T.; Matsuda, K. *Heterocycles* **1985**, *23*, 2489. Tsuge, O.; Kanemasa, S.; Yorozu, K.; Ueno, K. *Chem. Lett.* **1985**, 1601.

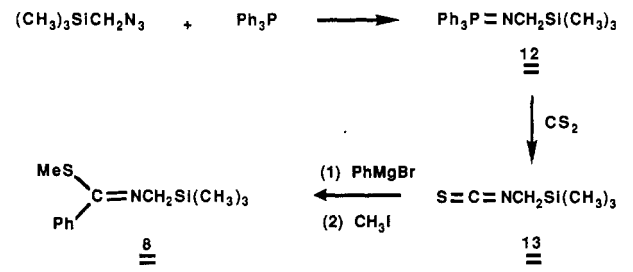
(31) Padwa, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 123.

(32) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 18.

(33) Padwa, A.; Kamigata, N. *J. Am. Chem. Soc.* **1977**, *99*, 1871.

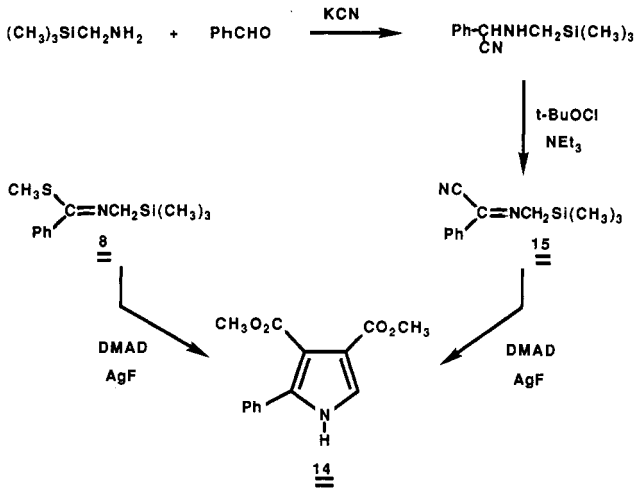


cleophilicity of the nitrile nitrogen atom to such a degree that it becomes unreactive toward the triflate reagent. The desired thioimidate could be conveniently prepared, however, by the reaction of phenyl-Grignard with (trimethylsilyl)methyl isothiocyanate (13). Addition of



methyl iodide to the resulting reaction mixture produced a 75% yield of 8. Isothiocyanate 13 was prepared by a two-step procedure starting from the known (trimethylsilyl)methyl azide.[34] Conversion of the azide to phosphorane 12 proceeded in 94% yield and this was followed by reaction with carbon disulfide to give isothiocyanate 13.

In a typical cycloaddition experiment, a solution of 8 and DMAD in acetonitrile was allowed to react in the dark with a slight excess of silver fluoride. Stirring was continued at room temperature for 12–18 h. The solvent was removed under reduced pressure to give 2-phenyl-3,4-dicarbomethoxypyrrole (14) in 85% yield. We also thought



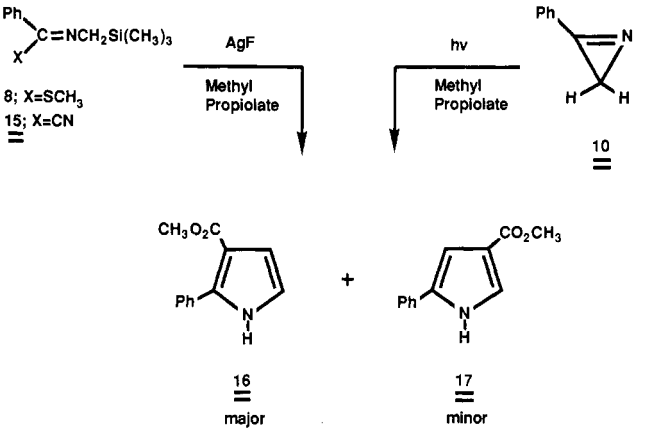
it worthwhile to determine whether an analogous reaction would occur upon changing the thiomethyl functionality for another leaving group. This led us to prepare cyano silyl imine 15. This material was obtained in two straight-forward steps by condensing (trimethylsilyl)methylamine with benzaldehyde in the presence of potassium cyanide. The initially formed cyano amine was oxidized by reaction with *tert*-butyl hypochlorite in the presence of triethylamine. Treatment of 15 with silver fluoride in the presence of DMAD under the standard conditions also gave pyrrole 14 in 73% yield.

(34) Tsuge, O.; Kanemasa, S.; Matsuda, K. *Chem. Lett.* **1983**, 1131; *J. Org. Chem.* **1984**, *49*, 2688.

Table I. Product Ratios for the Cycloaddition Reactions of Silyl Imidates 8 and 15 and Phenylazirine (10)

source	dipolarophile	product ratio
8	methyl propiolate	16:17 = 3.3/1
15	methyl propiolate	16:17 = 3.2/1
10	methyl propiolate	16:17 = 2.5/1
8	methyl acrylate	18:19 = 1.4/1
10	methyl acrylate	18:19 = 2.2/1
8	methyl methacrylate	20:21 = 6/1
10	methyl methacrylate	20:21 = 1.9/1
8	acrylonitrile	22:23 = 2.6/1
10	acrylonitrile	22:23 = 5/1
8	benzaldehyde	24:25 = 1/5
10	benzaldehyde	24 only
15	benzaldehyde	24:25 = 1/5

Information about the mechanistic details of the reaction has come from a study of the regiochemistry of cycloaddition of several unsymmetrically substituted systems. Treatment of 8 with silver fluoride in the presence of methyl propiolate produced a 3.3:1 mixture of pyrroles 16 and 17. The structure of the major product was estab-



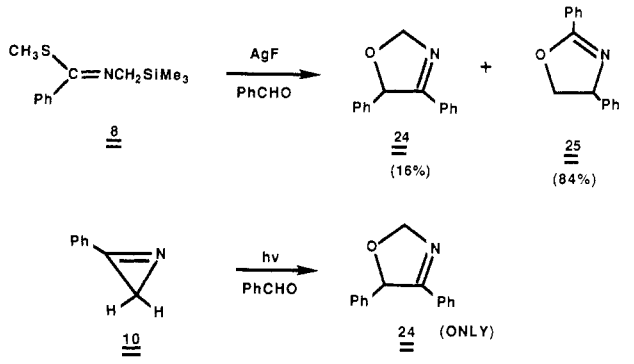
lished by comparison with an authentic sample.[35] Essentially the same mixture of pyrroles was obtained from the cyano silyl substituted imine 15. Interestingly, the ratio of the regioisomeric cycloadducts (i.e., 16 and 17) derived from the photolysis of phenylazirine (10) was slightly different from that obtained from the silyl imidate (16:17 = 2.5/1). This slight difference was well outside the experimental error used in determining the ratio of the two cycloadducts (360-MHz NMR and HPLC).

The cycloaddition reaction of 8 with a number of unsymmetrical dipolarophiles was also examined and the products formed are shown in Scheme I. The regiochemistry of the cycloadducts was established by comparison with authentic samples. In all cases, the ratio of the regioisomeric cycloadducts produced via the two methods differed (see Table I). The most dramatic difference occurred when benzaldehyde was used as the trapping agent. Treatment of 8 with silver fluoride in the presence of benzaldehyde produced a 1:5 mixture of dihydrooxazoles 24 and 25. In striking contrast, only oxazoline 24 was obtained when phenylazirine was irradiated in the presence of benzaldehyde.[36] No signs of oxazoline

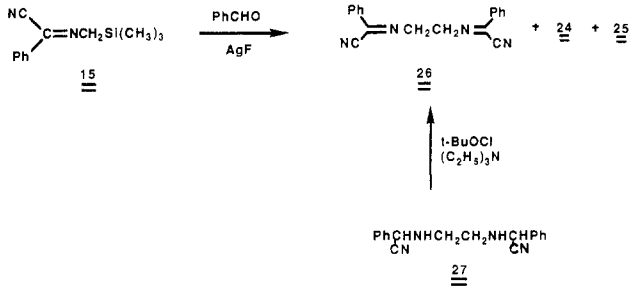
(35) Padwa, A.; Smolanoff, J.; Tremper, A. *J. Am. Chem. Soc.* **1975**, *97*, 4682.

(36) Giezendanner, H.; Marky, M.; Jackson, B.; Hansen, H., Jr.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 745; **1973**, *56*, 2611.

25 could be detected in the crude reaction mixture. Careful monitoring of the photoreaction (2–98% conversion) failed to give any indication of the presence of 25. Extended irradiation of 25 did not produce any detectable quantities of 24, thereby ruling out a subsequent rearrangement of 25 to 24.

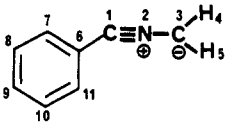


We also examined the reaction of cyano silyl imine 15 with benzaldehyde. Treatment of 15 with silver fluoride in the presence of benzaldehyde produced a mixture of three compounds. The major product isolated (65%) was assigned as the dicyano diimine 26. This assignment was



verified by comparison with an independently synthesized sample prepared by treating dicyano diamine 27 with *tert*-butyl hypochlorite in the presence of triethylamine. The two minor products were identified as oxazolines 24 and 25, which are formed in essentially the same ratio as that encountered with silyl thioimidate 8. The formation of dimer 26 can be rationalized in terms of a radical coupling reaction. Free radicals can be stabilized by both electron-acceptor and electron-donor groups.[37,38] Viehe has pointed out that radicals which are substituted simultaneously by a donor and acceptor substituent enjoy particular stabilization.[39] More than likely, the silver fluoride induced reaction of 15 with benzaldehyde proceeds in part via an electron-transfer step. This generates a captodative radical which undergoes subsequent coupling.[48]

Chart I. MNDO Parameters for Phenyl Nitrile Ylide 9



HOMO −7.45 eV
LUMO +1.42 eV

Coefficients - HOMO [C_1-(0.65); C_3-(0.69)]

LUMO [C_1-(0.48); C_3-(0.58)]

Heat Formation = 100.34 Kcal/mole

Dipole = 1.97 Debye

Distances (C_1-C_2=1.206A°; C_2-C_3=1.299A°)

Angles (C_6-C_1-C_2=152°; C_1-C_2-C_3=167°; C_2-C_3-C_4=120°)

It is well-known that the irradiation of 2*H*-azirines results in an irreversible ring opening and formation of nitrile ylides as transient intermediates.[3,4] Support for the existence of these species stems from pulsed laser photolysis experiments.[40] Irradiation of azirines in glassy matrices at 77 K results in the formation of new UV absorptions which are due to nitrile ylides.[40–42] Cycloadduct formation is derived from a thermal 1,3-dipolar addition of the initially generated nitrile ylide with the added dipolarophile. Frontier molecular orbital theory correctly rationalizes the regioselectivity of nitrile ylide cycloadditions.[43] When nitrile ylides are used as 1,3-dipoles, the dipole highest occupied (HOMO) and dipolarophile lowest unoccupied (LUMO) orbital interaction stabilizes the transition state.[44] The favored cycloadduct is that formed by the union of the atoms with the largest coefficients in the dipole HOMO and dipolarophile LUMO. An electron-deficient olefin has the largest coefficient on the unsubstituted carbon in the LUMO.[45] MNDO calculations of phenyl nitrile ylide 9 (Chart I) indicates that the coefficient size in both the HOMO and LUMO is slightly greater at the unsubstituted carbon atom. Thus, all the regiochemical results observed for the photocycloaddition of phenylazirine with electron-deficient alkenes and alkynes are perfectly compatible with the FMO predictions. Houk and Caramella[46] had previously carried out optimization of the geometry of the parent nitrile ylide and found that the dipole is bent with an H–C–N angle of 114–116°. They suggested that the most stable form of a nitrile ylide resembles a bent allenyl anion rather than a planar propargyl anion. Our recent MNDO calculations show that introduction of a phenyl group at C_1 drastically flattens the dipole (i.e., PhCN angle = 152°) and significantly lowers the energy separation between the linear and bent forms.

(37) Stella, L.; Janousek, Z.; Merenyi, R.; Viehe, H. G. *Angew. Chem.* **1978**, *90*, 741; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 691.

(38) Kaplan, L. *React. Intermed.* **1981**, *2*, 251.

(39) Viehe, H. G.; Merenyi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917.

(40) Turro, N. J.; Hrovat, D. A.; Gould, I. R.; Padwa, A.; Dent, W.; Rosentahl, R. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 625; *J. Org. Chem.* **1984**, *49*, 3174.

(41) Chapman, O.; LeRoux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 282.

(42) Orahovats, A.; Heimgartner, H.; Schmid, H.; Heinzelmann, W. *Helv. Chim. Acta* **1975**, *58*, 2662.

(43) Houk, K. N.; Sims, J.; Duke, R. E.; Strozier, R. W.; George, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287.

(44) Padwa, A.; Rasmussen, J. K.; Tremper, A. *J. Am. Chem. Soc.* **1976**, *98*, 2605.

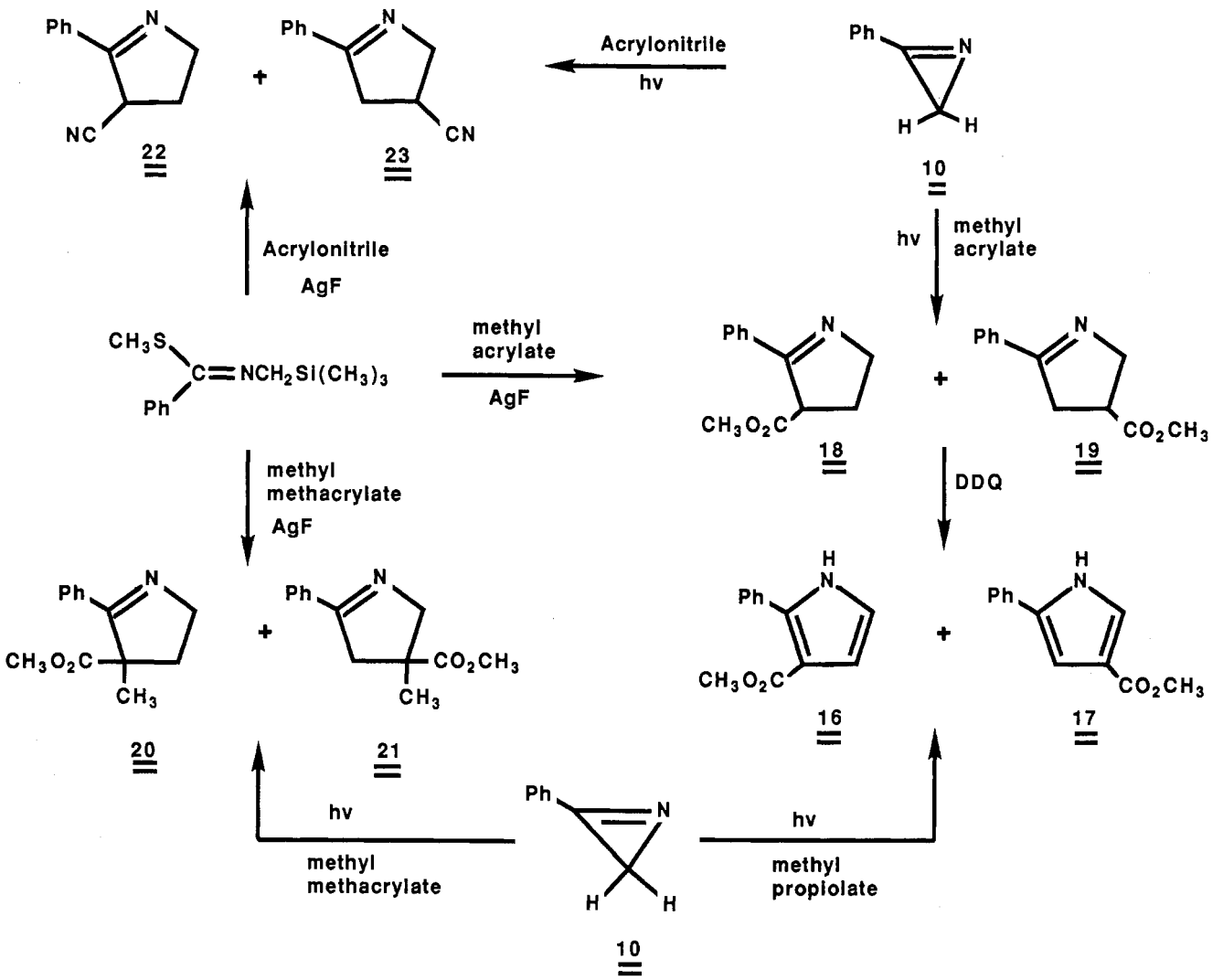
(45) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley-Interscience: New York, 1976.

(46) Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 6397. Caramella, P.; Gandour, R. W.; Hall, J. A.; Deville, G. G.; Houk, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 385.

(47) Tsuge, O.; Kanemasa, S.; Matsuda, K. *J. Org. Chem.* **1986**, *51*, 1997.

(48) There are several alternate mechanisms which could also account for the results. One possibility is that a small amount of methyl mercaptan reacts initially with silver fluoride to liberate hydrogen fluoride. N-Proto-C-desilylation of 8 (or 15) with HF could then give a N-protonated azomethine ylide. We find, however, that the reaction proceeds quite nicely in the presence of a proton scavenger (i.e., proton sponge). An alternate possibility is that thioimidate 8 is desilylated to give a 2-azaallyl anion[49] which undergoes conjugate addition to the added dipolarophile followed by displacement of thiophenoxide by the resulting carbanion. this mechanism was previously suggested to account for some of the results obtained with [1-(phenylthio)ethylidene]-1-(trimethylsilyl)methylamine.[16] The available data, however, do not distinguish between these various possibilities. Further work in regard to this point is in progress and will be reported on at a later point.

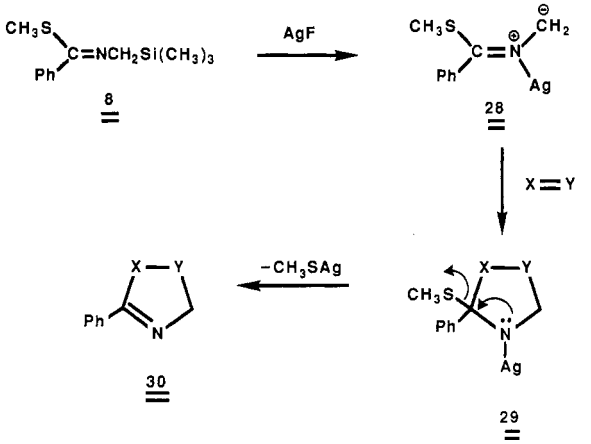
Scheme I



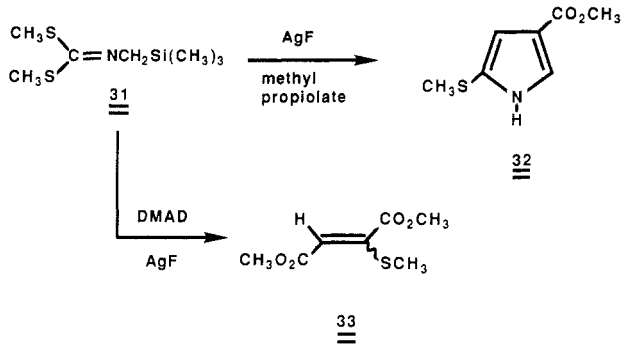
The MNDO calculations also suggest that the terminal carbon atom of nitrile ylide **9** should become linked with the carbonyl carbon atom of benzaldehyde since this represents the site of the largest LUMO coefficient. This prediction of regioselectivity is not, however, in agreement with the experimental results. Thus the cycloaddition of phenyl nitrile ylide with benzaldehyde must be related to other factors. Steric hindrance does not appear to play a role here since the more congested oxazoline **24** is formed. One possibility is that the regiochemistry is related to the charge-transfer energy of the cycloaddition. Benzaldehyde may induce an inhomogeneous electric field in the vicinity of the approaching dipole and van der Waal energy considerations may become important in determining regioselectivity.

We propose that the different product ratios encountered with silyl thioimidate **8** results from the operation of an alternate mechanism which does not involve a nitrile ylide intermediate. It seems likely that the silver ion complex of **8** leads to azomethine ylide **28** which is the species that actually cyclizes. This reactive intermediate would be expected to give ratios different than those from **9** in its 1,3-dipolar cycloaddition reactions (Scheme II). Recent work by Tsuge, Kanemasa, and Matsuda provides good support for the above mechanism.[47] These workers found that *N*-(silylmethyl)amidines and thioamides behave as nitrile ylide equivalents. Fluoride-induced desilylation of these silyl-substituted thioamides generate azomethine ylides which undergo successful cycloaddition with a variety of dipolarophiles. The resulting pyrrolidines readily eliminate the methylthio group and produce formal nitrile ylide cycloadducts.[48]

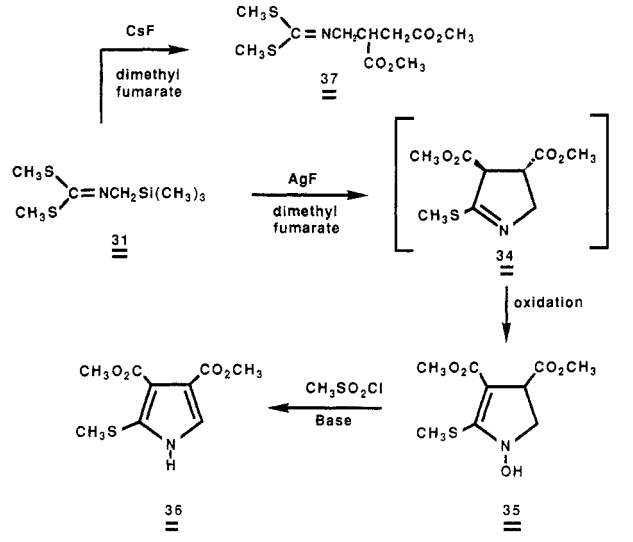
Scheme II



We have also examined the cycloaddition behavior of silyl imidocarbonate **31**. Reaction of **31** with methyl propiolate in the presence of silver fluoride proceeded smoothly and afforded pyrrole **32** in 63% yield. Attempts to obtain cycloadducts with other dipolarophiles were less successful. The reaction of **31** with DMAD afforded only the product resulting from addition of methyl mercaptan to the activated acetylene. The reaction of **31** with di-



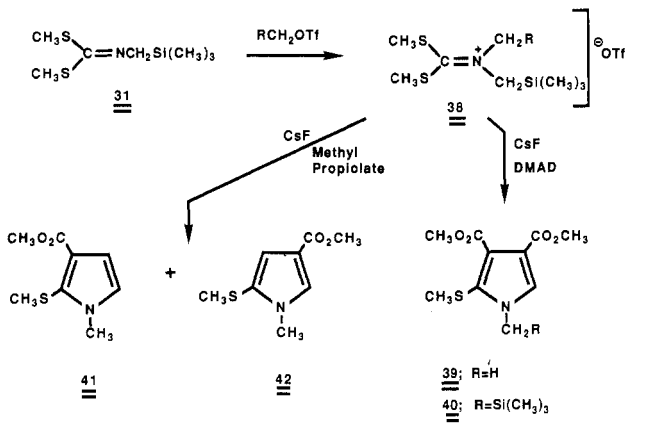
methyl fumarate in the presence of silver fluoride gave rise to the *N*-hydroxy-substituted dihydropyrrole **35**. The structure of this material was assigned on the basis of its analytical and spectral data (see Experimental Section) as well as by its conversion to pyrrole **36** upon treatment with mesyl chloride in the presence of base. Apparently, the initially formed cycloadduct **34** is readily oxidized by silver ion under the reaction conditions to the observed product. Interestingly, when silyl imidocarbonate **31** was



allowed to react with cesium fluoride in the presence of dimethyl fumarate, the only product isolated corresponded to imidocarbonate **37**. This reaction can be rationalized in terms of an initial desilylation to give a transient thioimidocarbonate anion which undergoes a subsequent conjugate addition to dimethyl fumarate. The above result clearly points out the need for the silver counterion for the [3 + 2]-cycloaddition to occur and is perfectly consistent with the mechanism outlined in Scheme II. Our efforts to trap the transient thioimidocarbonate anion with other electrophiles (alkyl halides, acid chlorides, esters) failed to produce the desired alkylated products.

Generation of an intermediate having azomethine ylide reactivity from imidocarbonate **31** was also achieved by treatment of **31** with methyl (or (trimethylsilyl)methyl) triflate, cesium fluoride, and an appropriate trapping reagent. Cycloaddition of the resulting dipole with DMAD produced pyrrole **39** (or **40**) in high yield, whereas reaction with methyl propiolate afforded a 1.5:1 mixture of pyrroles **41** and **42**.

In summary, the silver fluoride induced reaction of silyl thioimidates give formal nitrile ylide cycloadducts in good yield. The cycloaddition does not occur from a nitrile ylide intermediate but rather involves an azomethine ylide dipole derived from a silver-complexed imidate. This method allows access to a series of nonstabilized ylide dipoles and is currently being used in our laboratory to prepare



a number of naturally occurring products which possess the Δ^1-pyrroline ring system.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer Model 283 infrared spectrometer. Proton NMR spectra were obtained on Varian EM-390 and Nicolet FT-360 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*-[2-Phenyl-1-(phenylthio)ethylidene]-1-(trimethylsilyl)methylamine (3). A mixture containing 1.0 g of (trimethylsilyl)methyl triflate[50] and 0.50 g of freshly distilled phenylacetonitrile was heated for 25 min at 80 °C. At the end of this time the solution was cooled to 0 °C and was suspended in 10 mL of anhydrous benzene. The mixture was treated with a solution containing 0.46 g of thiophenol in 2 mL of anhydrous benzene and was stirred for 1 h at room temperature. The solution was poured into ice, extracted with ether, and washed with a 10% sodium carbonate solution. The organic phase was dried over magnesium sulfate and concentrated under reduced pressure to give a yellow oil. Silica gel chromatography of this material using a 20% ethyl acetate–hexane mixture as the eluent gave *N*-[2-phenyl-1-(phenylthio)ethylidene]-1-(trimethylsilyl)methylamine (**3**) as a clear oil: IR (neat) 3065, 3040, 2960, 2900, 1620, 1585, 1500, 1480, 1455, 1440, 1422, 1250, 1215, 1080, 1012, 1005, 860 and 750 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.07 (s, 9 H), 3.34 (s, 2 H), 3.52 (s, 2 H), 6.7–6.85 (m, 2 H), 6.95–7.1 (m, 3 H), 7.22 (s, 5 H); MS, *m/e* 313 (M^+), 253, 218, 204, 203, 118, 110, 109, 91, and 87; UV (95% ethanol) 254 nm (ϵ 6100) and 220 (16800). Anal. Calcd for $C_{18}H_{23}NSSi$: C, 68.96; H, 7.39; N, 4.47; S, 10.23. Found: C, 68.93; H, 7.24; N, 4.56; S, 10.39.

Reaction of *N*-[2-Phenyl-1-(phenylthio)ethylidene]-1-(trimethylsilyl)methylamine (3) with Dimethyl Acetylenedicarboxylate in the Presence of Silver Fluoride. A solution containing 720 mg of **3** and 640 mg of dimethyl acetylenedicarboxylate in 10 mL of dry acetonitrile was treated with 350 mg of silver fluoride. The mixture was stirred at room temperature for 16 h and was then filtered through Celite. The filter cake was washed with methylene chloride and the combined organic extracts were concentrated under reduced pressure. Flash chromatography of the crude residue using a 60% diethyl ether–hexane mixture as the eluent gave 230 mg (37%) of 2-benzyl-3,4-dicarbomethoxypyrrole (**4**) as a white crystalline solid: mp 142–143 °C; IR (KBr) 3300, 1720, 1530, 1460, 1440, 1300, 1290 (s), 1200, 1170, 1135, 1090, 1070 and 725 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 3.80 (s, 3 H), 3.83 (s, 3 H), 4.20 (s, 2 H), 7.10 (s, 1 H), 7.2–7.45 (m, 5 H), 8.60 (br s, 1 H); MS, *m/e* 273 (M^+), 242, 241, 210, 209, 181, 167,

(49) The fluoride-induced desilylation of *N*-silyl methyl imines has been studied by Tsuge and co-workers and was suggested to produce 2-azaallyl anions as transient species: Tsuge, O.; Kanemasa, S.; Hatada, A.; Matsuda, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2537.

(50) Ambasht, S.; Chiu, S. K.; Peterson, P. E.; Queen, J. *Synthesis* **1980**, 318.

155, 154, and 149; UV (95% ethanol) 261 nm (ε 8440) and 215 (18850). Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.83; H, 5.55; N, 5.13.

Preparation of *N*-[1-(Methylthio)benzylidene]-1-(trimethylsilyl)methylamine (8). A solution containing 5.0 g of (trimethylsilyl)methyl azide[34] in 10 mL of anhydrous ether was added to a stirred solution containing 10.2 g of triphenylphosphine in 50 mL of ether. The reaction mixture was stirred for 12 h at 25 °C until the evolution of nitrogen had ceased. The solvent was removed under reduced pressure to give 13.2 g (94%) of [([trimethylsilyl)methyl]imino]triphenylphosphorane (**12**) as a white solid: mp 92–93 °C; IR (KBr) 3070, 2950, 2900, 2800, 2750, 1600, 1490, 1445, 1405, 1395, 1305, 1245, 1205, 1150, 1100, 1025, 1000, 895, 850, and 750 cm^{-1}; NMR (CCl_4, 90 MHz) δ −0.95 (s, 9 H), 2.34 (rotomer a), 2.50 (rotomer b) (s, 2 H), and 7.4–7.8 (m, 15 H).

To a solution containing 2.0 g of the above compound in 50 mL of freshly distilled benzene was added a solution containing 0.84 g of carbon disulfide in 5 mL of benzene. The reaction mixture was heated at reflux for 2 h. The mixture was cooled to room temperature and the solvent was removed under reduced pressure to give 0.68 g (85%) of isocyanate **13** as a pale yellow liquid: bp 85–95 °C (15 mm); IR (neat) 2960, 2910, 2820, 2190, 2100, 1420, 1255, 1220, 1175, 850, 755, and 700 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.10 (s, 9 H) and 2.9 (s, 2 H).[34]

A solution containing 19 mL of 0.8 M phenylmagnesium bromide in tetrahydrofuran was added to 2.0 g of the above isocyanate. The reaction mixture was stirred at room temperature for 4 h and was then cooled to 10 °C and 2.0 g of methyl iodide was added. The reaction mixture was stirred overnight and the white precipitate that formed was filtered. To the resulting solution was added 20 mL of water and the mixture was extracted with ether. The ether layer was dried over magnesium sulfate and concentrated under reduced pressure to give 2.5 g (75%) of *N*-[1-(methylthio)benzylidene]-1-(trimethylsilyl)methylamine (**8**) as a pale yellow oil: bp 65–70 °C (0.02 mm); IR (neat) 3090, 3050, 2970, 2950, 2900, 2800, 1615, 1600, 1495, 1450, 1425, 1250, 1210, 1000, 955, 905, 860, and 770 cm^{-1}; NMR ($CDCl_3$, 90 MHz) minor isomer δ 0.02 (s, 9 H), 2.3 (s, 3 H), 3.1 (s, 2 H), and 7.2–7.5 (m, 5 H); major isomer 0.09 (s, 9 H), 1.97 (s, 3 H), 3.56 (s, 2 H), and 7.2–7.5 (m, 5 H); UV (95% ethanol) 250 nm (ε 5125), 257 (4625), and 264 (4180); MS, *m/e* 237 (M^+), 236, 192, 189, 160, 122, 120, 117, 92, 87, and 77; ^{13}C NMR ($CDCl_3$, 50 MHz) minor isomer δ −2.54 (q), 13.09 (q), 46.67 (t); major isomer 2.05 (q), 15.79 (q), 49.05 (t), 127.58, 128.18, 128.25, and 128.70. Anal. Calcd for $C_{12}H_{19}NSSi$: C, 60.70; H, 8.09; N, 5.90; S, 13.50. Found: C, 60.46; H, 8.11; N, 5.80; S, 13.59.

Preparation of Phenyl[[(trimethylsilyl)methyl]imino]acetonitrile (15). A solution containing 3.0 g of *N*-methyl(trimethylsilyl)amine[51] in 5 mL of ether was added dropwise to a stirred solution containing 3.1 g of benzaldehyde and 2.9 g of sodium bisulfite in 25 mL of water at 10 °C. The reaction mixture was stirred at 10 °C for 2 h. At the end of this time a solution containing 3.8 g of potassium cyanide in 10 mL of water was added dropwise and the mixture was stirred at room temperature for 5 h. The organic phase was separated and the aqueous layer was extracted with ether. The organic layer was dried over magnesium sulfate and was concentrated under reduced pressure to give 5.5 g (87%) of phenyl[[(trimethylsilyl)methyl]imino]acetonitrile as a yellow oil: IR (neat) 3340, 3090, 3050, 2980, 2900, 2800, 2230, 1640, 1600, 1500, 1450, 1420, 1250, 1200, 1100, 1075, 850, 800, and 700 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.02 (s, 9 H), 2.1 (d, 2 H, 3.0 Hz), 4.65 (s, 1 H), 7.2–7.5 (m, 5 H).

To a solution containing 1.0 g of the above material in 50 mL of anhydrous benzene at 5 °C was added a solution containing 0.6 g of *tert*-butyl hypochlorite in 5 mL of benzene. The reaction mixture was stirred at 5 °C for 30 min and then a solution containing 0.6 g of triethylamine in 5 mL of benzene was added. The reaction was stirred for 1 h at 5 °C and for 3 h at room temperature. Water was added and the mixture was extracted with ether. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography using a 9:1 mixture of hexane–ethyl acetate as the eluent. The product was obtained in 64% yield as a clear oil: IR (neat) 3125, 3020, 2960, 2895, 2300, 1600, 1525, 1490, 1480, 1350, 1320, 1295, 1200, 1185, 1175, 1010, 900, 815, and 720 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.01 (s, 9 H), 3.85 (s, 2 H), 7.29–7.46 and 7.8–7.97 (m, 5 H); MS, *m/e* 216 (M^+), 215, 204, 201, 179, 149, 118, 117, 116, 91, 90, and 77; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 0.01, 54.82, 109.99, 126.91, 128.82, 131.14, 134.20, and 137.64; UV (95% ethanol) 247 nm (ε 1870), 253 (2020), 258 (1950), and 263 (1650). Anal. Calcd for $C_{12}H_{16}N_2Si$: C, 66.62; H, 7.45; N, 12.95. Found: C, 66.65; H, 7.20; N, 12.70.

Reaction of Phenyl[[(trimethylsilyl)methyl]imino]acetonitrile (15) with Dimethyl Acetylenedicarboxylate in the Presence of Silver Fluoride. To a solution containing 300 mg of **15** and 198 mg of dimethyl acetylenedicarboxylate in 10 mL of anhydrous acetonitrile was added 206 mg of silver fluoride. The mixture was allowed to stir at 25 °C for 15 h. The precipitate that formed was filtered through Celite and the crude reaction mixture was concentrated under reduced pressure. The resulting residue was chromatographed on the chromatotron unit using a 3:1 hexane–ethyl acetate mixture as the eluent. The major fraction contained 260 mg (73%) of a white crystalline solid which was identified as 2-phenyl-3,4-dicarbomethoxypyrrole (**14**) on the basis of its spectral properties: mp 103–104 °C (lit.[52] mp 104–105 °C); NMR ($CDCl_3$, 90 MHz) δ 3.78 (s, 6 H), 7.15–7.4 (m, 5 H), and 9.40 (br s, 1 H); IR (KBr) 3300, 3150, 3050, 2965, 1735, 1690, 1515, 1500, 1450, 1410, 1350, 1270, 1205, 1105, 1060, 990, 940, 820, and 785 cm^{-1}; MS, *m/e* 259 (M^+), 228, 155, 149, 143, 131, 115, 108 (base), and 91; UV (95% ethanol) 275 nm (ε 10000). Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.84; H, 5.06; N, 5.38. The same pyrrole was produced in 85% when a sample of methylthio silyl imidate **8** was treated with silver fluoride in the presence of DMAD.

Reaction of *N*-[1-(Methylthio)benzylidene]-1-(trimethylsilyl)methylamine (8) with Methyl Propiolate in the Presence of Silver Fluoride. To a solution containing 300 mg of **8** and 120 mg of methyl propiolate in 10 mL of anhydrous acetonitrile was added 210 mg of silver fluoride. The mixture was allowed to stir at 25 °C for 15 h. The precipitate that formed was filtered through Celite and the crude reaction mixture was concentrated under reduced pressure. The residue was analyzed by NMR spectroscopy and was found to contain a 3.3:1.0 mixture of 2-phenyl-3-carbomethoxypyrrole (**16**) and 2-phenyl-4-carbomethoxypyrrole (**17**). The isomers were separated by silica gel column chromatography using a 3:1 hexane–ethyl acetate mixture as the eluent. The major isomer obtained was identified as 2-phenyl-3-carbomethoxypyrrole (**16**) (77% yield) by comparison with an authentic sample:[35] NMR ($CDCl_3$, 90 MHz) δ 3.67 (s, 3 H), 6.62 (br s, 1 H), 6.66 (br s, 1 H), 7.2–7.6 (m, 5 H), and 8.5 (br s, 1 H).

The minor isomer was identified as 2-phenyl-4-carbomethoxypyrrole (**17**) (23%) on the basis of its spectral data; mp 168–169 °C; IR (KBr) 3400–3200, 3025, 3010, 2950, 2870, 1680, 1610, 1580, 1520, 1495, 1455, 1445, 1400, 1385, 1355, 1280, 1220, 1145, 1130, 1100, 925, 830, and 770 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 3.85 (s, 3 H), 6.92 (m, 2 H), 7.26–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 51.13 (s), 106.74 (s), 117.90, 124.16, 127.12, 129.05, 131.81, and 133.17; MS, *m/e* 201 (M^+), 200, 171, 170, 160, 149, 115, 105, 104, and 97; UV (95% ethanol) 255 nm (ε 2290), 260 (7340), and 2870 (17430). Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.39; H, 5.55; N, 6.91.

The same mixture of 2-phenyl-3-carbomethoxy (**16**) and 2-phenyl-4-carbomethoxypyrrole (**17**) (3.2:1) was obtained by treating cyano imine **15** with methyl propiolate in the presence of silver fluoride. The ratio of pyrroles **16**:**17** was 2.5:1 when phenylazirine (**10**) was irradiated with methyl propiolate for 2 h in benzene by using a Vycor filter sleeve.

Reaction of *N*-[1-(Methylthio)benzylidene]-1-(trimethylsilyl)methylamine (8) with Methyl Acrylate in the Presence of Silver Fluoride. To a solution containing 300 mg of **8** and 120 mg of methyl acrylate in 10 mL of anhydrous acetonitrile was added 210 mg of silver fluoride. The mixture was allowed to stir at 25 °C for 15 h. The resulting precipitate was filtered through Celite and the crude reaction mixture was con-

(51) Sommer, L. H.; Rockett, J. *J. Am. Chem. Soc.* **1951**, *73*, 5130.

(52) Apsimon, J. W.; Durham, D. G.; Rees, A. H. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1588.

centrated under reduced pressure. The residue was analyzed by NMR spectroscopy and was found to contain a 1:1.4 mixture of 2-phenyl-4-carbomethoxy-Δ^1-pyrroline (**19**) and 2-phenyl-3-carbomethoxy-Δ^1-pyrroline (**18**).[5]

The crude reaction mixture was taken up in 15 mL of anhydrous benzene and was treated with 1.0 equiv of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. The mixture was heated at 80 °C for 6 h. The resulting black solution was concentrated under reduced pressure and was analyzed by NMR spectroscopy. The NMR spectrum showed the presence of 2-phenyl-4-carbomethoxypyrrole (**17**) (60%) and 2-phenyl-3-carbomethoxypyrrole (**16**) (40%). The isomers were separated by silica gel chromatography and were found to be identical with the material isolated from the reaction of **8** with methyl propiolate in the presence of silver fluoride.

Irradiation of phenylazirine (**10**) in benzene containing an equivalent amount of methyl acrylate for 2 h gave rise to a 1:2.2 mixture of 2-phenyl-4-carbomethoxy-Δ^1-pyrroline (**19**) and 2-phenyl-3-carbomethoxy-Δ_1-pyrroline (**18**) as determined by the integration of the carbomethoxy singlets located at 3.67 and 3.57 ppm, respectively.

Reaction of *N*-[1-(Methylthio)benzylidene]-1-(trimethylsilyl)methylamine (8) with Methyl Methacrylate in the Presence of Silver Fluoride. To a solution containing 300 mg of **8** and 130 mg of methyl methacrylate in 10 mL of anhydrous acetonitrile was added 210 mg of silver fluoride. The mixture was allowed to stir at 25 °C for 15 h. The precipitate that formed was filtered through Celite and the crude reaction mixture was concentrated under reduced pressure. The residue was analyzed by NMR spectroscopy and was found to contain a 6:1 mixture of 2-phenyl-3-carbomethoxy-3-methyl-Δ^1-pyrroline (**20**) and 2-phenyl-4-carbomethoxy-4-methyl-Δ^1-pyrroline (**21**). The isomers were separated by silica gel chromatography using a 10% ethyl acetate–hexane mixture as the eluent. The minor isomer eluted from the chromatotron unit was identified as 2-phenyl-4-carbomethoxy-4-methyl-Δ^1-pyrroline (**21**) (14%) by comparison with an authentic sample:[5] NMR ($CDCl_3$, 360 MHz) δ 1.40 (s, 3 H), 2.90 (ddd, 1 H, J = 19.5, 2.2, and 0.8 Hz), 3.60 (ddd, 1 H, J = 19.5, 2.2, and 2.0 Hz), 3.99 (ddd, 1 H, J = 16.5, 2.2, and 0.8 Hz), 4.39 (ddd, 1 H, J = 16.5, 2.2, and 2.0 Hz), 7.4–7.6 (m, 3 H), and 7.8–7.9 (m, 2 H). The major isomer was identified as 2-phenyl-3-carbomethoxy-3-methyl-Δ^1-pyrroline (**20**) (86%) by comparison with an authentic sample:[5] NMR ($CDCl_3$, 360 MHz) δ 1.52 (s, 3 H), 2.04 (ddd, 1 H, J = 13.0, 8.3, and 5.1 Hz), 2.53 (ddd, 1 H, J = 13.0, 8.7, and 6.5 Hz), 4.0–4.3 (m, 2 H), 7.4–7.6 (m, 3 H), and 7.7–7.8 (m, 2 H).

Irradiation of phenylazirine (**10**) in benzene containing an equivalent amount of methyl methacrylate for 2 h gave rise to a 1.9:1 mixture of 2-phenyl-3-carbomethoxy-3-methyl-Δ^1-pyrroline (**20**) and 2-phenyl-4-carbomethoxy-4-methyl-Δ^1-pyrroline (**21**).

Reaction of *N*-[1-(Methylthio)benzylidene]-1-(trimethylsilyl)methylamine (8) with Acrylonitrile in the Presence of Silver Fluoride. To a solution containing 250 mg of **8** and 60 mg of acrylonitrile in 8 mL of anhydrous acetonitrile was added 180 mg of silver fluoride. The mixture was allowed to stir at 25 °C for 15 h. The NMR spectrum of the crude reaction mixture showed the presence of 2-phenyl-3-cyano-Δ^1-pyrroline (**22**) and 2-phenyl-4-cyano-Δ^1-pyrroline (**23**) in a ratio of 2.6:1. The isomers were separated by silica gel chromatography using a 3:1 hexane–ethyl acetate mixture as the eluent. The first fraction contained 2-phenyl-4-cyano-Δ^1-pyrroline (**23**) (30%) which was identified by comparison with an authentic sample:[5] mp 95–96 °C; NMR ($CDCl_3$, 360 MHz) δ 3.2–3.5 (m, 3 H), 4.25–4.55 (m, 2 H), 7.15–7.4 (m, 3 H), 7.53–7.78 (m, 2 H); UV (95% ethanol) 245 nm (ϵ 12 400).

The second fraction contained 2-phenyl-3-cyano-Δ^1-pyrroline (**22**) (70%): mp 151–152 °C; IR (KBr) 3100, 3000, 3030, 2990, 2950, 2885, 2200, 1625, 1595, 1495, 1480, 1450, 1390, 1310, 1280, 1200, 2200, 1625, 1595, 1495, 1480, 1450, 1390, 1310, 1280, 1200, 1150, 1120, 1100, 1000, 790, and 755 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.4–2.85 (m, 3 H), 3.4–3.5 (m, 1 H), 4.0–4.17 (m, 1 H), 7.38–7.54 (m, 3 H), and 8.09–8.11 (m, 2 H); UV (95% ethanol) 255 nm (ϵ 7760) and 280 (7230). Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92. Found: C, 77.67; H, 5.64.

Irradiation of phenylazirine (**10**) in benzene containing an equivalent amount of acrylonitrile for 2 h gave rise to a 5:1 ratio of Δ^1-pyrrolines **22** and **23**.

Reaction of *N*-[1-(Methylthio)benzylidene]-1-(trimethylsilyl)methylamine (8) with Benzaldehyde in the Presence of Silver Fluoride. To a solution containing 300 mg of **8** and 140 mg of benzaldehyde in 10 mL of anhydrous acetonitrile was added 210 mg of silver fluoride. The mixture was allowed to stir at 25 °C for 15 h. The resulting precipitate was filtered through Celite and the crude reaction mixture was concentrated under reduced pressure. The residue was subjected to silica gel chromatography using a 10% ethyl acetate–hexane mixture as the eluant. The minor isomer (14%) was identified as 4,5-diphenyl-3-oxazoline (**24**) by comparison with an authentic sample:[36] NMR ($CDCl_3$, 360 MHz) δ 5.81 (dd, 1 H, J = 12.0 and 3.4 Hz), 5.88 (dd, 1 H, J = 12.0 and 5.6 Hz), 6.06 (dd, 1 H, J = 5.6 and 3.4 Hz), 7.2–7.45 (m, 8 H), and 7.65–7.8 (m, 2 H).

The major isomer obtained from the column (70%) was identified as 2,5-diphenyl-2-oxazoline (**25**) on the basis of its spectral data:[53] IR (neat) 3095, 3050, 2950, 2895, 1650, 1605, 1590, 1500, 1450, 1345, 1255, 1090, 1060, 1020, and 950 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 4.0 (dd, 1 H, J = 15.0 and 8.1 Hz), 4.5 (dd, 1 H, J = 15.0 and 9.9 Hz), 5.65 (dd, 1 H, J = 9.9 and 8.1 Hz) 7.3–7.55 (m, 8 H), 7.9–8.1 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 63.26 (t), 81.14 (d), 125.72, 128.25, 128.38, 128.82, 131.32; UV (95% ethanol) 240 nm (ϵ 18 950); MS, m/e 223 (M^+), 118, 117, 116, 110, 91, 90, 89, 78, and 77.

Irradiation of a sample of phenylazirine (**10**) in benzene containing an equivalent amount of benzaldehyde for 2 h gave rise to 4,5-diphenyl-3-oxazoline (**24**) as the exclusive photoproduct. No signs of the isomeric oxazoline **25** were present in the crude reaction mixture.

Reaction of Phenyl[[(trimethylsilyl)methyl]imino]-acetonitrile (15) with Benzaldehyde in the Presence of Silver Fluoride. To a solution containing 600 mg of **15** and 300 mg of benzaldehyde in 10 mL of anhydrous acetonitrile was added 400 mg of silver fluoride. The mixture was allowed to stir at 25 °C for 15 h. The precipitate that formed was filtered through Celite and the crude reaction mixture was concentrated under reduced pressure. The resulting residue was subjected to silica gel chromatography using a 10% ethyl acetate–hexane mixture as the eluent. The major fraction contained 240 mg (65%) of a yellow crystalline solid whose structure was assigned as (ethylenedinitrilo)bis[phenylacetonitrile] (**26**) on the basis of its spectral properties and by an independent synthesis: mp 183–184 °C; IR (KBr) 2945, 2880, 2225, 1610, 1600, 1580, 1497, 1480, 1450, 1320, 1297, 1278, 1045, 1026, and 775 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 4.43 (s, 4 H), 7.4–7.6 (m, 6 H), 7.85–8.1 (m, 4 H); UV (95% ethanol) 268 nm (ϵ 19 500), 218 (13 400); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 58.11, 127.70, 127.79, 128.90, 129.08, 129.23, 132.38, and 133.49. The two minor fractions isolated from the column contained 2,5-diphenyl-2-oxazoline (**25**) and 4,5-diphenyl-3-oxazoline (**24**) in a 5:1 ratio.

Independent Synthesis of (Ethylenedinitrilo)bis[phenylacetonitrile] (26). To a solution containing 5.0 g of ethylenediamine in 100 mL of absolute ethanol were added 14.8 g of benzaldehyde, 11.1 g of potassium cyanide, and 10 g of acetic acid. The solution was stirred for 5 h at room temperature, at which time the mixture turned into a thick white slurry. This mixture was poured into 100 mL of water and extracted with chloroform. The chloroform layer was dried over magnesium sulfate and the solvent was removed under reduced pressure to give 13 g of *N,N'*-[bis(cyanobenzyl)]ethylenediamine **27** was a white solid: mp 121–122 °C; IR (KBr) 3345, 3310, 2920, 2850, 2200, 1500, 1455, 1270, 1130, 930, and 740 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.72 (s, 2 H), 2.97 (s, 4 H), 4.75 (s, 2 H), 7.2–7.5 (m, 10 H).

To a solution containing 3.0 g of the above material in 75 mL of anhydrous benzene was added a solution containing 2.3 g of *tert*-butyl hypochlorite in 10 mL of anhydrous benzene at 0 °C. The mixture was stirred at room temperature for 2 h. At the end of this time the solution was cooled to 0 °C and 2.3 g of triethylamine was added. The orange solution was stirred for 2 h at room temperature and was then poured into water and extracted with chloroform. The chloroform layer was dried over magnesium sulfate and the solvent was removed under reduced pressure to give (ethylenedinitrilo)bis[phenylacetonitrile] (**26**) as

(53) Butt, M. I.; Neilson, D. G.; Watson, K. M.; Ullah, Z. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2328.

a yellow crystalline solid, mp 121–122 °C, whose spectral properties were identical with those obtained from the material isolated from the reaction of **15** with benzaldehyde in the presence of silver fluoride.

Preparation of Dimethyl [(Trimethylsilyl)methyl]carbonimidodithioate (31). To a solution containing 3.0 g of (trimethylsilyl)methylamine[49] and 2.0 g of sodium hydroxide in 10 mL of water was added 4.0 g of carbon disulfide. The reaction mixture solidified almost immediately and the colorless precipitate was collected by filtration, washed with cold ether, and dried to give 4.25 g (72%) of a white solid. This material was suspended in 20 mL of dichloromethane and a solution containing 7.8 g of methyl triflate in 20 mL of dichloromethane was added dropwise at 0 °C. Addition of the triflate at higher temperatures led to the elimination of methyl mercaptan and the formation of isothiocyanate. After being stirred at 25 °C for 6 h, the reaction mixture was stirred with a 10% sodium hydroxide solution and was then extracted with chloroform. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure to give a pale yellow oil (74%). Chromatography of this material on the chromatotron unit with hexane as the eluent gave a pure sample of dimethyl [(trimethylsilyl)methyl]carbonimidodithioate (**31**): IR (neat) 2960, 2930, 2900, 1655, 1580, 1425, 1310, 1250, 1210, 1000, 960, 850, 760, and 700 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.15 (s, 9 H), 2.35 (s, 3 H), 2.60 (s, 3 H), 3.40 (s, 2 H); UV (methanol) 220 nm (ϵ 8390) and 257 (9260). Anal. Calcd for $C_7H_{17}NS_2Si$: C, 40.58; H, 8.21; N, 6.76. Found: C, 40.52; H, 8.26; N, 6.74.

Reaction of Carbonimidodithioate 31 with Methyl Propiolate as the Dipolarophile. The reaction of carbonimidodithioate **31** with methyl propiolate gave rise to a single product, mp 69–70 °C (63%), whose structure was assigned as 2-(methylthio)-4-carbomethoxypyrrole (**32**) on the basis of its spectral properties: IR (KBr) 3290, 3110, 2960, 1695, 1555, 1480, 1440, 1250, 1205, 1180, 1145, 1000, and 770 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.38 (s, 3 H), 3.90 (s, 3 H), 6.78 (dd, 1 H, J = 2.5 and 1.6 Hz), 7.50 (dd, 1 H, J = 3.0 and 1.6 Hz), 9.45 (br s, 1 H); UV (methanol) 255 (ϵ 9990); MS, m/e 171 (M^+, base), 156, 140, 125, 12, 97, 85, and 70. Anal. Calcd for $C_7H_9NO_2S$: C, 49.12; H, 5.30; N, 8.18. Found: C, 49.25; H, 5.32; N, 8.16.

Reaction of Carbonimidodithioate 31 with Dimethyl Fumarate as the Dipolarophile. When dimethyl fumarate was used as the dipolarophile, a single compound was isolated in 34% yield as a white crystalline solid, mp 124–125 °C, whose structure was assigned as dimethyl 2,3-dihydro-1-hydroxy-2-(methylthio)-1*H*-pyrrole-3,4-dicarboxylate (**35**) on the basis of the following spectral data: IR (KBr) 3140 (br), 2970, 1745, 1730, 1600, 1450, 1370, 1295, 1205, 1150, 1060, 1000, 950, 890, and 780 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.43 (s, 3 H), 3.57 (t, 1 H, J = 9.0 Hz), 3.78 (s, 3 H), 3.81 (s, 3 H), 4.05 (dd, 1 H, J = 14.8 and 9.0 Hz), 4.19 (s, 1 H), 4.35 (dd, 1 H, J = 14.8 and 9.0 Hz); UV (methanol) 242 nm (ϵ 7580), 270 (5950); MS, m/e 247 (M^+), 229, 188, 115, 87 (base), and 72. Anal. Calcd for $C_9H_{13}NO_5S$: C, 43.73; H, 5.30; N, 5.64. Found: C, 43.72; H, 5.30; N, 5.64.

The structure of this material was verified by its conversion to 2-(methylthio)-3,4-dicarbomethoxypyrrole (**36**). To a solution containing 120 mg of **35** in 5 mL of dichloromethane were added 1 mL of triethylamine and 0.5 mL of mesyl chloride. The reaction mixture turned red and was mildly exothermic when the mesyl chloride was added. Stirring was continued for 5 h and then the reaction mixture was washed with water and extracted with chloroform. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column using a 2:1 hexane–ether mixture as the eluent to give 90 mg (81%) of **36**: mp 92–93 °C; IR (KBr) 3270, 3130, 3000, 2950, 1720, 1685, 1550, 1495, 1440, 1285, 1200, 1170, 1120, 1060, 980, 780, 760, and 730 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.35 (s, 3 H), 3.75 (s, 3 H), 3.83 (s, 3 H), 7.25 (d, 1 H, J = 3.0 Hz), 9.80 (br s, 1 H); UV (methanol) 268 nm (ϵ 11 500). Anal. Calcd for $C_9H_{11}NO_4S$: C, 47.11; H, 4.80; N, 6.11. Found: C, 47.18; H, 4.86; N, 6.09.

The reaction of carbonimidodithioate **31** with dimethyl fumarate using cesium fluoride as the desilylating agent was also studied. Under these conditions, dimethyl [(2,3-dimethoxycarbonyl)propyl]carbonimidodithioate (**37**) was isolated (42%) as a colorless oil. A pure sample of **37** was obtained by silica gel chromatography using a 10% ether–hexane mixture as the eluent: IR (neat) 3000, 2960, 2870, 1740, 1580, 1435, 1360, 1160, 1000, 980, 895, and 840 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.32 (s, 3 H), 2.55 (s, 3 H), 2.65 (dd, 1 H, J = 17.0 and 5.4 Hz), 2.86 (dd, 1 H, J = 17.0 and 8.6 Hz), 3.21 (dtd, 1 H, J = 8.6, 5.9, and 5.4 Hz), 3.60 (d, 2 H, J = 5.9 Hz), 3.70 (s, 3 H), 3.75 (s, 3 H); UV (methanol) 220 nm (ϵ 8390), 257 (9260). Anal. Calcd for $C_{10}H_{17}NO_4S_2$: C, 43.01; H, 6.14; N, 5.02. Found: C, 43.13; H, 6.17; N, 5.01.

Reaction of Dimethyl [(Trimethylsilyl)methyl]carbonimidodithioate (31) with Methyl Triflate and Cesium Fluoride. To a sample containing 415 mg of carbonimidodithioate **31** in 10 mL of anhydrous methylene chloride was added 330 mg of methyl triflate. After stirring at 25 °C for 16 h, 285 mg of dimethyl acetylenedicarboxylate and 330 mg of cesium fluoride were added to this solution. Stirring was continued for another 12 h and then the reaction mixture was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The crude residue was chromatographed on a silica gel column using a 2:1 hexane–ether mixture as the eluent to give 66% of *N*-methyl-2-(methylthio)-3,4-dicarbomethoxypyrrole (**39**) as a colorless solid: mp 61–62 °C; IR (KBr) 3120, 2940, 1695, 1685, 1565, 1435, 1350, 1210, 1180, 1145, 1000, 820, and 770 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.32 (s, 3 H), 3.70 (s, 3 H), 3.78 (s, 3 H), 3.95 (s, 3 H), 7.30 (s, 1 H); UV (methanol) 263 nm (ϵ 14 480); MS, m/e 243 (M^+), 212 (base), 211, 210, 197, 182, 180, 179, 166, 153, 139, 125, and 69. Anal. Calcd for $C_{10}H_{13}NO_4S$: C, 49.38; H, 5.39; N, 5.76. Found: C, 49.45; H, 5.40; N, 5.74.

When (trimethylsilyl)methyl triflate was used as the alkylating reagent, the major cycloadduct isolated (54%) was a pale yellow oil whose structure was assigned as *N*-[(trimethylsilyl)methyl]-2-(methylthio)-3,4-dicarbomethoxypyrrole (**40**) on the basis of its spectral properties: IR (neat) 3120, 2960, 1720, 1535, 1505, 1440, 1350, 1270, 1250, 1210, 1165, 1095, 1050, 860, and 770 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.10 (s, 9 H), 2.27 (s, 3 H), 3.70 (s, 2 H), 3.75 (s, 3 H), 3.87 (s, 3 H), 7.20 (s, 1 H); UV (methanol) 218 nm (ϵ 9750), 257 (24 220). Anal. Calcd for $C_{13}H_{21}NO_4SSi$: C, 49.46; H, 6.66; N, 4.44. Found: C, 49.53; H, 6.75; N, 4.43.

In addition to this material, pyrrole **39** was also present in the reaction mixture (25%). Treatment of **40** with cesium fluoride resulted in its desilylation and formation of *N*-methylpyrrole **39**.

Treatment of Dimethyl [(Trimethylsilyl)methyl]carbonimidodithioate (31) with Methyl Triflate in the Presence of Methyl Propiolate. To a sample containing 400 mg of carbonimidodithioate **31** in 10 mL of methylene chloride was added 340 mg of methyl triflate. After stirring at 25 °C for 15 h, 270 mg of methyl propiolate and 320 mg of cesium fluoride was added. Standard workup of the mixture gave rise to a 1.5:1 mixture (72% overall yield) of two cycloadducts. These compounds were separated by silica gel chromatography using a 30% hexane–ether mixture as the eluent. The major compound obtained was assigned the structure of *N*-methyl-2-(methylthio)-3-carbomethoxypyrrole (**41**) on the basis of its spectral properties: IR (neat) 3000, 2950, 2930, 1700, 1530, 1490, 1400, 1370, 1350, 1235, 1195, 1170, 1125, 1040, 930, and 800 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.35 (s, 3 H), 3.69 (s, 3 H), 3.82 (s, 3 H), 6.59 (AB quartet, 2 H, J = 3.2 Hz); UV (methanol) 237 nm (ϵ 7700) and 278 (5800).

The minor component was assigned the structure of *N*-methyl-2-(methylthio)-4-carbomethoxypyrrole (**42**) on the basis of its spectral properties: IR (neat) 3000, 2960, 2920, 1710, 1550, 1445, 1380, 1360, 1220, 1115, 1060, 1000, 840, 800, and 765 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.25 (s, 3 H), 3.65 (s, 3 H), 3.80 (s, 3 H), 6.70 (d, 1 H, J = 1.9 Hz), 7.35 (d, 1 H, J = 1.9 Hz).

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health and the National Science Foundation. Use of the high-field NMR spectrometer used in these studies was made possible through a NSF equipment grant.

Supplementary Material Available: Experimental details for the preparation and attempted intramolecular cycloaddition reactions of methyl *N*-[(trimethylsilyl)methyl]-5-hexenimidothioate (**5**) and [[(trimethylsilyl)methyl]imino]-*o*-vinylhydrocinnamonitrile (**6**) (6 pages). Ordering information is given on any current masthead page.