Conclusion

This study fails to support bicycloaromaticity as a significant factor in determining radical cation structures. In contrast, homoaromaticity is seen to provide stabilization to the extent that the intramolecular [3 + 2] cycloaddition of $3^{\bullet+}$ to homoaromatic $15^{\bullet+}$ is extremely rapid. This system is the second example of a homoaromatic radical cation structure type. As with several other recent examples from our laboratory, we note that the potential energy surfaces of radical cation and the corresponding neutral parent may be substantially different. In this paper we have shown that the equilibrium between two structures (**3** and **15**) is shifted dramatically on the radical cation surface. The chemistry of organic radical cations continues to be an exciting area of study.

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Carbene and Silicon Routes as Methods for the Generation and Dipolar Cycloaddition Reactions of Methyl Nitrile Ylide

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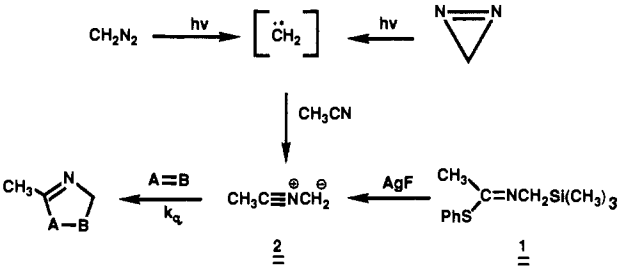
Abstract: Methyl nitrile ylide was generated by both a photochemical and desilylation route and has been characterized by UV spectroscopy and by its kinetic and cycloaddition behavior. The dipole is formed by the addition of singlet methylene to acetonitrile and shows a strong transient absorption at 280 nm which is quenched by the addition of standard dipolarophiles. The relative rates of formation of 1,3-dipolar adducts and the relative rates of quenching of the transient absorption are in excellent agreement. Generation of the dipole from a silylthioimidate followed by dipolar cycloaddition also gave rise to related cycloadducts. The ratio of cycloadducts obtained from an unsymmetrically substituted dipolarophile was found to be strikingly dependent on the purity of the silylthioimidate. The different product ratios result from the operation of an alternate mechanism which involves the thiophenol that is released in the decomposition of silylthioimidate to the nitrile ylide. The initially generated dipole is believed to react with excess thiophenol to give a "half-capped" dipole which undergoes a subsequent conjugate addition to the unsymmetrical dipolarophile.

The widespread use of the 1,3-dipolar cycloaddition reaction stems in part from the frequent need to synthesize five-membered heterocyclic rings and the customarily high efficiency of such cycloadditions.[1-4] One of the more interesting members of the 1,3-dipole family is the nitrile ylides.[5] This class of dipoles has traditionally been prepared by (a) treatment of imidoyl halides with base,[6] (b) thermal or photochemical elimination of phosphoric acid esters from 4,5-dihydro-1,3,5-oxazaphospholes,[7] and (c) photolysis of aryl-substituted azirines.[8-10] More recently, nitrile ylides have been observed to be formed upon photolysis of carbene precursors in nitrile solvents. The nitrile ylides formed in this manner have been trapped by olefinic dipolarophiles.[11-14] 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 discovered two new and general methods for nitrile ylide formation. Generation of an intermediate having nitrile ylide reactivity was achieved from the photolysis of diazomethane or diazirine in acetonitrile. The 1,3-dipole formed in this manner can be readily trapped with a variety of dipolarophiles to give cycloadducts in high yields. An alternate route to the same dipole involves desilylation of an appropriately substituted nitrilium cation. Thus, silylthioimidate **1** serves as a convenient nitrile ylide precursor and undergoes smooth dipolar cycloaddition with a variety of dipolarophiles in the presence of silver fluoride according to Scheme I.

Scheme I



Results and Discussion

Pulsed excimer laser photolysis of diazirine (ca. 0.003 M) or diazomethane (ca. 0.05 M) in air-saturated acetonitrile at room temperature produced a transient absorption ($\tau > 100$ μs) with λ_{max} at 280 nm (Figure 1). This transient is not observed in the absence of acetonitrile or the methylene precursor. On the basis

Table I. Rate Constants for the Reactions of Methyl Nitrile Ylide with Various Quenchers at 298 K in Air-Saturated Acetonitrile

quencher	k_q, M^{-1} s^{-1}[a]
maleic anhydride	$(4.5 \pm 0.3) \times 10^9$
fumaronitrile	$(2.18 \pm 0.08) \times 10^9$
diethyl fumarate	$(7.9 \pm 0.3) \times 10^8$
dimethyl acetylenedicarboxylate	$(1.5 \pm 0.1) \times 10^8$
diethyl maleate	$(5.7 \pm 0.3) \times 10^7$
benzaldehyde	$(3.2 \pm 0.2) \times 10^7$
acrylonitrile	$(5.6 \pm 0.2) \times 10^6$
methyl acrylate	$(3.28 \pm 0.07) \times 10^6$
methyl propiolate	$(4.4 \pm 0.3) \times 10^5$

[a] Pulsed laser photolysis (Lambda Physik EMG 101 Excimer Laser, 308 nm, 20 ns) of diazirine (ca. 0.003 M) in air-saturated acetonitrile.

* Dedicated to Cheves Walling on the occasion of his 70th birthday.
† Emory University.
‡ Columbia University.

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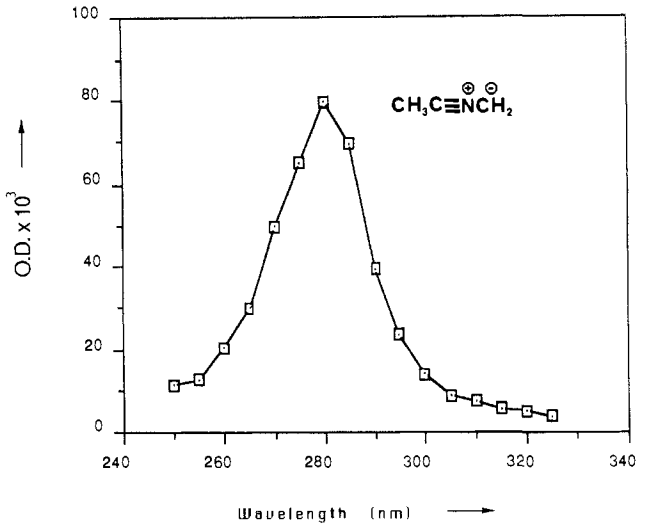
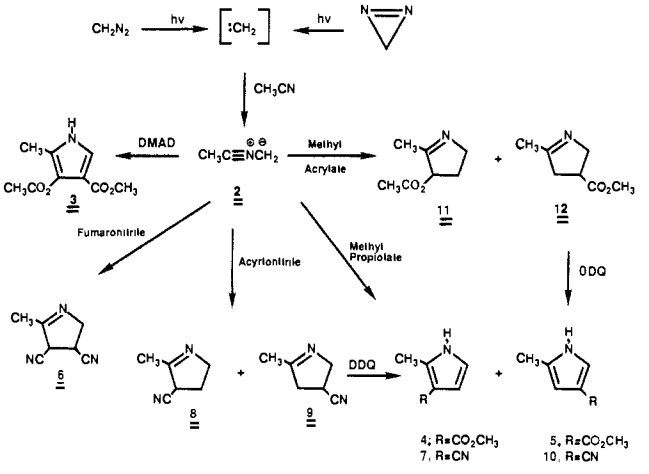


Figure 1. Transient absorption spectrum obtained 2.5 μs after pulsed laser photolysis of diazirine (ca. 0.003 M) in air-saturated CH_3CN.

Scheme II



of the products formed and by comparison with the absorption spectra of other nitrile ylides,[10] the intense absorption at 280 nm is assigned as methyl nitrile ylide **2**. This dipole is formed by electrophilic attack of singlet methylene onto the lone-pair of electrons on the nitrogen atom of acetonitrile (Scheme I).

The quenching behavior of the methyl nitrile ylide obtained from the photolysis of diazirine in acetonitrile was studied by the addition of a series of dipolarophiles. As was noted earlier, nitrile ylides were quenched efficiently by electron-deficient olefins. In fact, the decay of the absorption spectrum of the nitrile ylide derived from pulsed laser photolysis of diazirine in air-saturated acetonitrile solution followed clean first-order kinetics at high olefin concentration. Bimolecular quenching rate constants, k_q, were

Table II. Product Yield and Relative Rate Data for the Cycloaddition Reaction of Methyl Nitrile Ylide

quencher	k_{rel}[a] (time-resolved)	k_{rel}[b] (prod. anal.)	yield, %
fumaronitrile	390 ± 30	430 ± 60	43
dimethyl acetylenedicarboxylate	27 ± 2	42 ± 10	45
acrylonitrile	1.0	1.0	56
methyl acrylate	0.6 ± 0.1	0.7 ± 0.1	50
methyl propiolate	0.08 ± 0.01	0.10 ± 0.01	47

[a] Data calculated from Table I. [b] Steady-state photolysis (1000-W Xe–Hg lamp, Pyrex) of diazirine (ca. 0.012–0.018 M) in air-saturated acetonitrile at 0 °C.

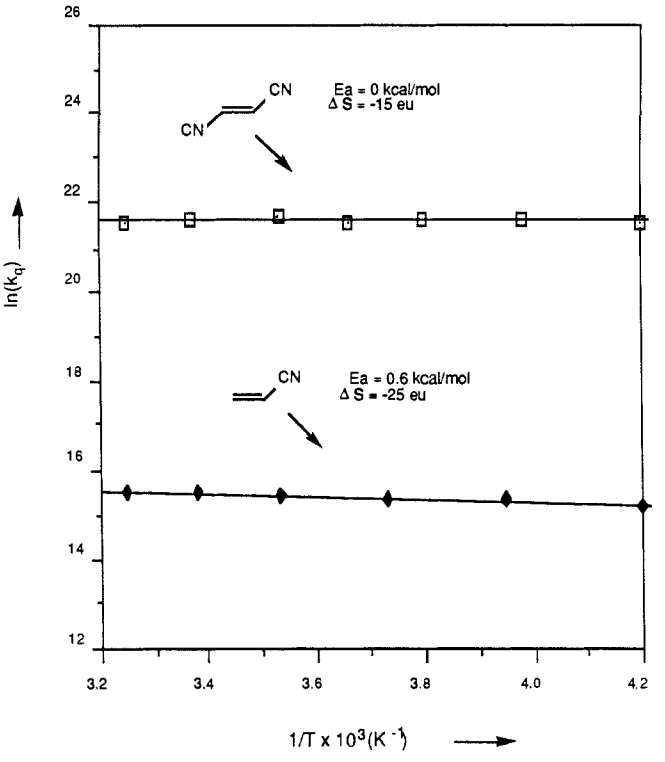


Figure 2. Arrhenius plot for the quenching of methyl nitrile ylide derived from flash laser photolysis of diazirine in CH_3CN by acrylonitrile and fumaronitrile.

obtained from the slopes of plots of the observed first-order rate for ylide decay vs. olefin concentration. The quenching rate constants for several olefins and other quenchers in acetonitrile are listed in Table I. The kinetic quenching rate constants obtained by using acrylonitrile and fumaronitrile as quenchers are consistent with the reactivity observed with related nitrile ylides.[10]

Steady-state photolysis of diazirine or diazomethane in acetonitrile was investigated in the presence of various dipolarophiles. In a typical experiment, a solution containing diazirine (ca. 0.02 M) and acrylonitrile (ca. 1.0 M) in acetonitrile was irradiated through Pyrex with a 1000-W Xe–Hg lamp at 0 °C. The regiochemistry of the cycloaddition reaction was established by DDQ oxidation of the crude reaction mixture to the corresponding pyrroles. The identity of the pyrroles was established by comparison of their NMR and IR spectra with authentic samples (see Experimental Section). The products formed are shown in Scheme II. The ratio of the two regioisomers derived from the nitrile ylide cycloaddition with an unsymmetrical dipolarophile, such as acrylonitrile, methyl acrylate, or methyl propiolate, was ca. 1:1. Irradiation using diazomethane as the methylene precursor was carried out at −40 °C in acetonitrile in order to reduce the rate of addition of diazomethane to electron-deficient olefins.[15] The

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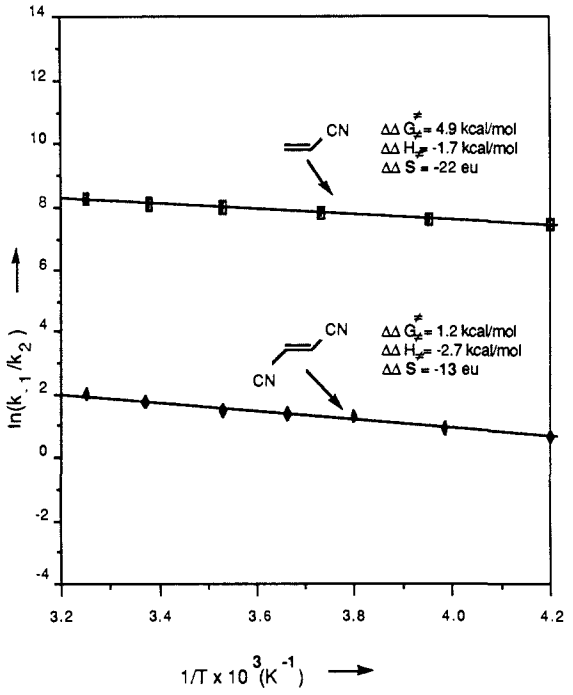

Figure 3. Plot of ln (k_{-1}/k_2) vs. $1/T$ (K) ($\Delta\Delta G^{\ddagger}$ calculated at 298 K).

product yields for several dipolarophiles and the relative quenching rates obtained from the absolute rate constants and steady-state trapping experiments are summarized in Table II. As expected, the relative rates of cycloadduct formation and the relative rates of quenching the transient absorption are within experimental error. The quenching rate constants (k_q) for the reaction of the methyl nitrile ylide with acrylonitrile and fumaronitrile were determined as a function of temperature (238–308 K). The Arrhenius plots shown in Figure 2 are for k_q after correction of the quencher concentrations due to solvent contraction. The value of k_q is essentially insensitive to temperature for fumaronitrile (E_a = 0 kcal/mol), while for acrylonitrile a small positive (E_a = 0.6 kcal/mol) activation energy is observed. Zero or small temperature effects have been observed previously for several different reactions,[16] including those of nitrile ylides.[10] This behavior has previously been explained as being consistent with an ylide/olefin intermediate complex (eq 1). In this case k_q is given by eq 2.

$$NY + O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NY/O \xrightarrow{k_2} \text{products} \qquad (1)$$

Assuming that k_1 is equal to the rate of diffusive encounter of the ylide and the olefin,[10,16] then the value of (k_{-1}/k_2) can be

$$k_q = \frac{k_1 k_2}{k_{-1} + k_2} \qquad (2a)$$

$$\frac{k_1 - k_q}{k_q} = \frac{k_{-1}}{k_2} \qquad (2b)$$

$$\ln (k_{-1}/k_2) = \Delta\Delta G^{\ddagger}/RT \qquad (2c)$$

$$\Delta\Delta G^{\ddagger} = \Delta\Delta H^{\ddagger} - T\Delta\Delta S^{\ddagger} \qquad (2d)$$

determined by eq 2b. The $\Delta\Delta G^{\ddagger}$ in eq 2c is the difference in the free energies for product formation and dissociation from the complex ($\Delta\Delta G^{\ddagger} = \Delta G^{\ddagger}_2 - \Delta G^{\ddagger}_{-1}$). Plots of ln (k_{-1}/k_2) vs. $1/T$ yield $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ and are shown in Figure 3.

Two other nitrile ylides have also been observed upon pulsed laser photolysis of diazirine in the presence of large quantities of nitriles. Transient absorption spectra of dipoles **13** and **14** have been detected by laser flash photolysis of diazirine in isobutyronitrile (5.5 M) and benzonitrile (2 M) in pentane. The quenching rate constants of these two ylides by electron-deficient olefins are comparable to that of methyl nitrile ylide **2** (Table III). These results suggest that the formation of nitrile ylides by the combination of methylene with nitriles may be a general phenomenon.

Table III. Spectroscopic and Rate Constant Data for Nitrile Ylides **2**, **13**, and **14** at 298 K

	2	**13**	**14**
λ_{max} at 298 K, nm	280	280	*a*
k_q, M^{-1} s^{-1} (fumaronitrile)[b]	2.18 ± 0.08 × 10^9	2.14 ± 0.06 × 10^9	1.63 ± 0.09 × 10^9
k_q, M^{-1} s^{-1} (acrylonitrile)	5.6 ± 0.2 × 10^6	3.57 ± 0.07 × 10^6	2.2 ± 0.1 × 10^6
k_q, M^{-1} s^{-1} (methyl acrylate)	3.28 ± 0.07 × 10^6	2.0 ± 0.1 × 10^6	1.2 ± 0.1 × 10^6

[a] λ_{max} could not be determined for this ylide because of the strong absorption of benzonitrile below 290 nm. [b] Same conditions as in *a* of Table I.

$(CH_3)_2CHC{\equiv}\overset{\oplus\ominus}{N}CH_2$ (**13**) $PhC{\equiv}\overset{\oplus\ominus}{N}CH_2$ (**14**)

In searching for alternate ways to generate nitrile ylides, we investigated the silver fluoride induced desilylation of silylthioimidate **1**. The development of this method was based on literature reports that formamidines and imidoyl halides can function as nitrilium ion precursors.[17-19] The desilylation of α-trimethylsilyl onium salts by fluoride ion has been widely utilized in recent years as a convenient method for preparing nitrogen and sulfur ylides.[20-32] By far the most extensively studied application of the desilylation method is in the generation of azomethine ylides.[20,25-29] Relatively little work had been done, however, using the trimethylsilyl functionality as a leaving group for the generation of nitrile ylides. One example which probably proceeds via a nitrile ylide has recently been reported by Tsuge.[33] The isolation of pyrroline **19** from the desilylation of the N-protonated amidinium salt **17** suggests the involvement of a nitrile ylide intermediate (i.e., **18**). This sequence involves a fluoride ion induced elimination of *N*-methylaniline followed by formation of nitrile ylide **18**.

Cyclization reactions which involve the closure of nitrilium cations onto carbon-centered nucleophiles have recently been reported by Livinghouse.[17] The requisite nitrilium ions were prepared via the silver ion mediated ionization of α-ketoimidoyl halides synthesized by the reaction of organic isonitriles with acyl halides. This observation suggests that treatment of thioimidates

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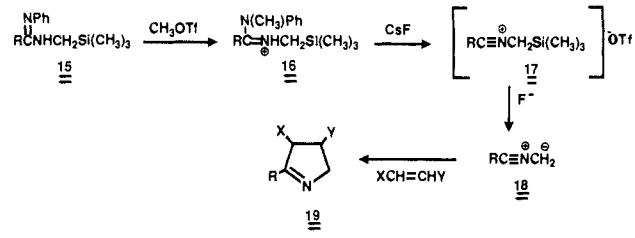
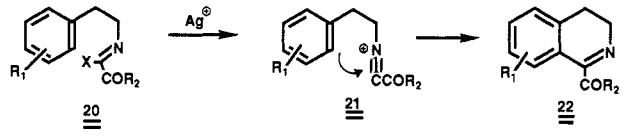
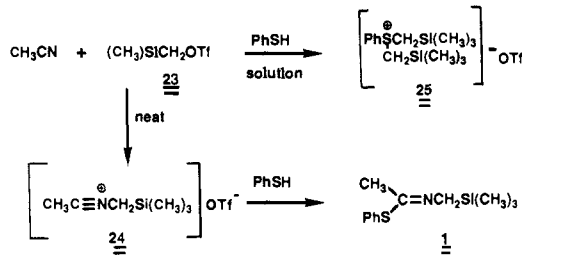


with silver ion would result in the formation of a nitrilium ion.[34]

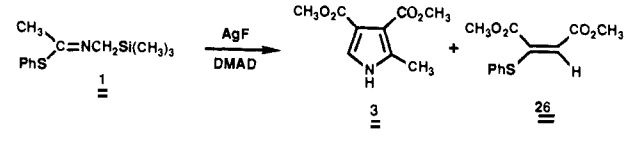


The propensity of silicon to transfer to a silylophile when bound to an electronegative carbon also suggested that the reaction of silylthioimidate **1** with silver fluoride would generate methyl nitrile ylide. In spite of its simplicity and its obvious potential as a nitrile ylide equivalent, silylthioimidate **1** could not be found in the literature. This reagent was conveniently prepared in multigram quantities by heating equimolar quantities of acetonitrile and (trimethylsilyl)methyl triflate at 70 °C for 10 min. The resulting nitrilium salt **24** was then suspended in benzene and treated with thiophenol to form silylthioimidate **1** in quantitative yield. The



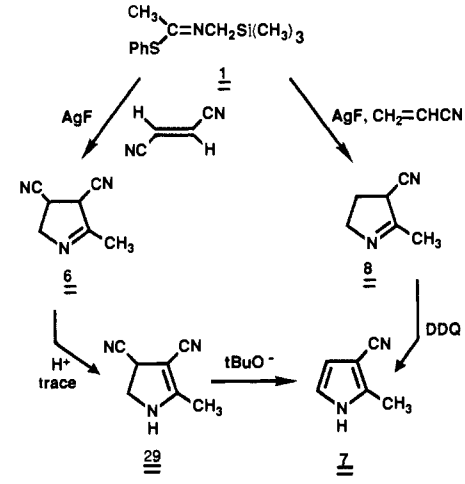
short reaction time and absence of solvent was found to be critical in order to obtain high yields of **1**. Attempts to prepare **1** by heating a solution of (trimethylsilyl)methyl triflate and acetonitrile in benzene for short periods of time followed by the addition of thiophenol only led to the formation of sulfonium salt **25**.

In a typical cycloaddition experiment, a solution of **1** and dimethyl acetylenedicarboxylate in acetonitrile was allowed to react in the dark with a slight excess of silver fluoride. Stirring



was continued at room temperature for 12 h. The black precipitate that formed was filtered, and the solvent was removed under reduced pressure to give 2-methyl-3,4-dicarbomethoxypyrrole (**3**) (60%) as well as a cis–trans mixture of dimethyl 2-(phenylthio)-2-butenedioate (**26**). The use of 2 equiv of the dipolarophile was necessary in order to maximize the yield due to the facile conjugate addition of thiophenoxy anion onto the electron-deficient dipolarophile.[35]

It was of interest to compare the results for the cycloaddition of nitrile ylide **2** by the "carbene" route to those of reaction of **2** by the "desilylation procedure". The reaction of the nitrile ylide derived from **1** with acrylonitrile afforded a single adduct **8** whose regiochemistry was established as the 2,3-isomer by DDQ oxidation to pyrrole **7**. No signs of the isomeric 2,4-disubstituted pyrrole **10** were found in the crude reaction mixture. An authentic sample of 2-methyl-4-cyanopyrrole (**10**) was independently synthesized by treating the TOSMIC reagent with acrylonitrile according to the procedure of Van Leusen.[36] 2-Methyl-3-cyanopyrrole (**7**) was also prepared by treating silylthioimidate **1** with fumaronitrile. The initially formed cycloadduct **6** tautomerized



to structure **27** which formed pyrrole **7** upon treatment with potassium *tert*-butoxide. This result stands in contrast to the regioselectivity encountered from the photolysis of diazirine (or diazomethane) in acetonitrile where a 1:1 mixture of cycloadducts was formed when acrylonitrile was used as the trapping reagent.

All attempts to obtain a cycloadduct from the reaction of **1** with nonactivated olefins (i.e., cyclohexene, 1-octene, norbornene, etc.) failed.[37] Our inability to isolate a 1,3-cycloadduct with these systems is consistent with the principles of frontier MO theory.[38] When nitrile ylides are used as 1,3-dipoles, the dipole highest occupied (HOMO) and dipolarophile lowest unoccupied (LUMO) interactions will be of greatest importance in stabilizing the transition state. Placement of an electron-withdrawing substituent on the π-bond of an alkene will lower both the HOMO and LUMO orbital energies of the olefin and consequently facilitate the rate of the 1,3-dipolar cycloaddition reaction. The favored cycloadduct will be that formed by union of the atoms with the largest coefficient in the dipole HOMO and dipolarophile LUMO.[38]

We also examined the cycloaddition behavior of **1** with other unsymmetrically substituted dipolarophiles so as to further probe the regioselectivity of the cycloaddition. Treatment of a freshly prepared sample of silylthioimidate **1** with silver fluoride in the presence of methyl propiolate produced a 2:3 mixture of pyrroles **4** and **5**. The structures of these compounds were established by comparison with independently synthesized samples. The 2,3-isomer **4** was prepared by the hydrogenation of *N*-benzylpyrrole **28**, while the 2,4-isomer **5** was synthesized by a transesterification reaction of the known ethyl ester **29**.

Although these results suggest the commonality of methyl nitrile ylide **2** as an intermediate via the carbene or silicon route, the ratio of the regioisomeric cycloadducts (i.e., **4** and **5**) derived from methyl propiolate via the two methods differed. For example, the ratio of pyrroles produced from the carbene route (1:1) was slightly different from that obtained from silylimidate **1** (**4**:**5** =

(34) One of the reviewers has suggested that the silver ion complex of **20** is what actually cyclizes rather than intermediate **21** with its sp-hybridized nitrogen. It is conceivable that silver fluoride might work in a similar way with the thioimidates. Thus, some of the reactions reported might involve a silver-complexed imidate and an azomethine ylide dipole which could rationalize some of the regiochemistry effects (i.e., **4** and **31** from **1**). Loss of mercaptan could occur after the cycloaddition. Another possibility is that thiophenol reacts initially with silver fluoride to liberate small quantities of HF. N-Proto-C-desilylation of **1** with HF then gives the corresponding N-protonated azomethine ylide in analogy with Tsuge.[33] This species would be expected to give ratios different than those from **2** in its 1,3-dipolar cycloaddition reactions.

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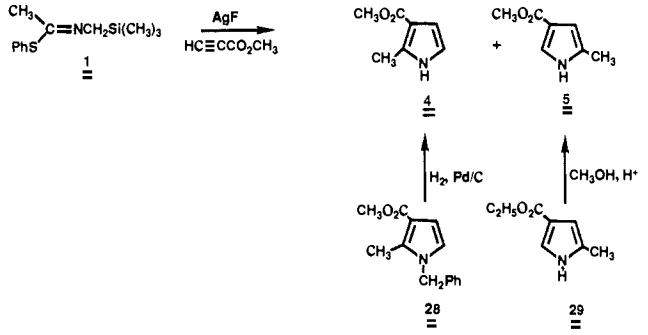
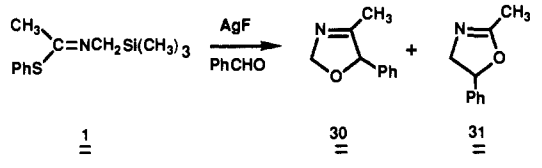
(37) Nitrile ylides generated from the photolysis of azirines also do not undergo cycloaddition with nonactivated dipolarophiles.[8,9]

(38) Houk, K. N.; Sims, J. H.; Duke, R. E.; Strozier, R. W.; George, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287; **1973**, *95*, 7301; **1973**, *95*, 5798; Padwa, A.; Smolanoff, J. *J. Chem. Soc., Chem. Commun.* **1973**, 342.

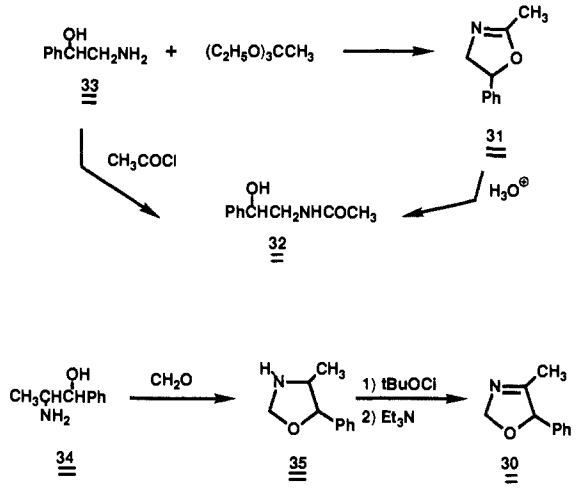


2:3). This slight difference was well outside the experimental error used in determining the ratio of the two cycloadducts. Most importantly, the ratio of the cycloadducts was found to be strikingly dependent on the purity of the silylthioimidate **1**. For example, the ratio of pyrroles **4** and **5** changed from 2:3 to 9:1 when an aged sample of **1** was used.

A similar variation in product ratio was also encountered in the reaction of silylthioimidate **1** with benzaldehyde. Treatment of **1** with silver fluoride in the presence of benzaldehyde afforded a 3:2 mixture of dihydrooxazoles **30** and **31**. Attempts to separate



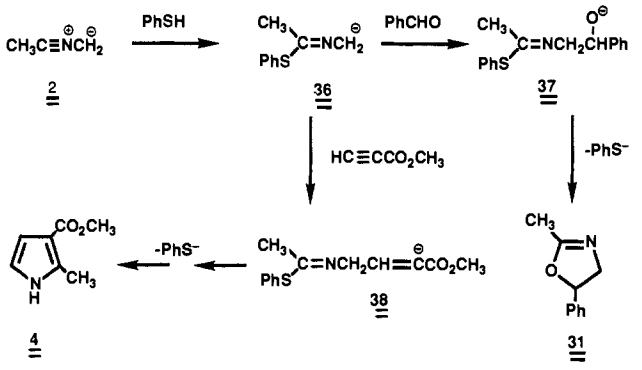
the two regioisomers resulted in the hydrolytic conversion of **31** into hydroxy amide **32**. The structure of **32** was established by comparison with a sample prepared from the acylation of 2-amino-1-phenylethanol (**33**). Dihydrooxazole **31** was also prepared by treating **33** with triethyl orthoacetate. The other regioisomer,



30, was independently synthesized by treating the known isoxazoline **35** with *tert*-butyl hypochlorite followed by reaction of the resulting *N*-chloroamine with triethylamine. As was the case with methyl propiolate, the ratio of the cycloadducts was strikingly dependent on the purity of silylthioimidate **1**. Thus, the ratio of the dihydrooxazoles changed from 3:2 to 1:10 when impure samples of thioimidate **1** were used.

We propose that the different product ratios result from the operation of an alternate mechanism which involves the thiophenol that is released in the decomposition of silylthioimidate to nitrile ylide **2**. When pure samples of thioimidate **1** are used, the cycloadditions proceed via the nitrile ylide dipole. This is supported by the fact that essentially the same ratio of regioisomeric cycloadducts is obtained from the silicon approach as from the carbene route. Aged samples of silylthioimidate **1**, on the other hand, contain significant quantities of thiophenol as a consequence of aqueous hydrolysis. Most likely, the initially generated nitrile ylide reacts with the excess thiophenol to give carbanion **36**.

Scheme III



Stepwise addition of this species to benzaldehyde or methyl propiolate followed by intramolecular cyclization nicely rationalizes the product variation. In fact, thiophenol-doped samples of pure thioimidate **1** give rise to pyrrole **4** and dihydrooxazole **31**, supporting the mechanism outlined in Scheme III.[34]

In summary, methyl nitrile ylide can be formed by the addition of singlet methylene to acetonitrile. The methyl nitrile ylide generated in this fashion has been characterized by its kinetic quenching behavior and the formation of cycloaddition products with a variety of dipolarophiles. Addition of singlet methylene to isobutyronitrile and benzonitrile produced isopropyl nitrile ylide and phenyl nitrile ylide, respectively. The silver fluoride induced desilylation reaction of thiosilylimidates also provides ready access to the reactive nitrile ylide in synthetically useful yields. The ratio of cycloadducts obtained when unsymmetrically substituted dipolarophiles are used is dependent on the concentration of thiophenol present in solution. Control of the regiochemistry of cycloaddition will considerably broaden the use of these compounds in organic synthesis.

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 283 infrared spectrometer. ^{1}H NMR spectra were obtained on Varian EM-390 and Nicolet FT-360 spectrometers. ^{13}C NMR spectra were recorded on an IBM 200-MHz spectrometer. Microanalyses were performed at Atlantic Microlabs, Atlanta, GA. Mass spectra were determined with a Finnegan 4000 mass spectrometer at an ionizing voltage of 70 eV.

Acetonitrile (MCB, OmniSolv) was used as supplied. Isobutyronitrile and benzonitrile were distilled. The olefin and acetylene quenchers were purified by passage through neutral alumina and distillation prior to use. Fumaronitrile was purified by sublimation. Maleic anhydride was recrystallized from carbon tetrachloride and was then purified by sublimation. Diazirine[39] and diazomethane[40] were synthesized in the corresponding solvent immediately before use. The laser flash photolysis system is the same as previously described.[10] Diazirine was excited at 308 nm (XeCl, 20-ns pulse), while diazomethane was excited at 351 nm (XeF, 15-ns pulse).

Preparation of [1-(Phenylthio)ethylidene]-1-(trimethylsilyl)methylamine (1). A mixture containing 1.00 g of (trimethylsilyl)methyl triflate and 0.17 g of acetonitrile in 8 mL of anhydrous benzene was heated at 75 °C for 20 min. The solution was cooled to 0 °C and was then treated with a solution containing 0.46 g of thiophenol in 2 mL of anhydrous benzene. After stirring for 1 h at room temperature, the solution was poured into ice and extracted with ether. The organic phase was washed with a 10% sodium carbonate solution, dried over magnesium sulfate, and concentrated under reduced pressure to give a white crystalline solid whose structure was assigned as bis[(trimethylsilyl)methyl)]phenylsulfonium triflate (**25**) on the basis of its spectral properties; mp 160–161 °C; IR (KBr) 2950, 2900, 1380, 1260, 1225, 1150, 1030, 860, and 755 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ −0.07 (s, 18 H), 3.07 (d, 2 H, J = 13.5 Hz), 3.37 (d, 2 H, J = 13.5 Hz), 7.6–7.8 (m, 3 H), and 8.02–8.17 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ −1.86, 29.16, 34.31, 129.84, 130.72, 131.21, and 134.89; UV (95% ethanol) 273 nm (ϵ 6000), 266 (ϵ 6100), 259 (ϵ 5300), and 220 (ϵ 8300); mass spectrum, *m/e* 149 and 111. Anal.

(39) Ohme, R.; Schmitz, E. *Chem. Ber.* **1964**, *97*, 297.
(40) Arndt, F. *Organic Synthesis*; Wiley: New York, 1943; Collect. Vol. 2, p 165.

Calcd for $C_{15}H_{27}F_3O_3S_2Si_2$: C, 41.64; H, 6.29; S, 14.82. Found: C, 41.63; H, 6.32; S, 14.81. This material could also be prepared by simply heating a mixture of thiophenol and (trimethylsilyl)methyl triflate in benzene.

In order to avoid salt formation, the following conditions were used. A mixture containing 1.00 g of (trimethylsilyl)methyl triflate and 0.17 g of acetonitrile was heated for 10 min at 70–80 °C. At the end of this time the mixture was cooled to 0 °C and *N*-[(trimethylsilyl)methyl]-acetonitrilium triflate (**24**) crystallized as a lightly colored yellow solid. This material was suspended in 10 mL of anhydrous benzene and was treated dropwise with a solution containing 0.46 g of thiophenol in 2 mL of anhydrous benzene. After stirring for 1 h at room temperature, the solution was poured into ice and extracted with ether. The organic phase was washed with a 10% sodium carbonate solution, dried over magnesium sulfate, and concentrated under reduced pressure to give 1.0 g (100%) of a pale-yellow oil. Chromatography of this material on a silica gel column using a 4% ethyl acetate–hexane mixture as the eluent gave [1-(phenylthio)ethylidene]-1-(trimethylsilyl)methylamine (**1**) as a clear oil: IR (neat) 2965, 2940, 2905, 2870, 1630, 1590, 1482, 1442, 1430, 1370, 1250, 1217, 1130, 1093, 1060, 1028, 924, 855, and 750 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.10 (s, 9 H), 1.79 (s, 3 H), 3.28 (s, 2 H), and 7.25–7.55 (m, 5 H); UV (95% ethanol) 255 nm (ϵ 5500), 221 (ϵ 17 860); mass spectrum, *m/e* 237 (M^+), 236, 222, 181, 165, 130, 129, 128, 87, and 72; ^{13}C NMR ($CDCl_3$, 50 MHz) δ −1.98, 26.50, 47.44, 128.70, 129.08, 131.79, 135.03, 135.50, and 155.00. Anal. Calcd for $C_{12}H_{19}NSSi$: C, 60.71; H, 8.07; N, 5.90; S, 13.50. Found: C, 60.78; H, 8.11; N, 5.89; S, 13.43.

Reaction of [1-(Phenylthio)ethylidene]-1-(trimethylsilyl)methylamine (1) with Dimethyl Acetylenedicarboxylate in the Presence of Silver Fluoride. A stirred solution containing 500 mg of **1** and 600 mg of dimethyl acetylenedicarboxylate in 7 mL of anhydrous acetonitrile was treated with 350 mg of silver fluoride. The mixture was stirred at room temperature in the dark for 12 h and was then filtered through a Celite column. The filter cake was washed with methylene chloride, and the solvent was removed under reduced pressure. The resulting residue was chromatographed on a silica gel column using a 10% ethyl acetate–hexane mixture as the eluent. The first and second fractions contained diphenyl disulfide and a cis–trans mixture of dimethyl 2-(phenylthio)-2-butenedioate (**26**):[41] NMR ($CDCl_3$, 90 MHz) δ cis isomer 3.58 (s, 6 H), 5.46 (s, 1 H), and 7.25–7.6 (m, 5 H); trans isomer 3.29 (s, 3 H), 3.75 (s, 3 H), 6.3 (s, 1 H), and 7.2–7.72 (m, 5 H); mass spectrum, *m/e* 252 (M^+), 221, 193, 192, 161, 149, 134, 109, and 77.

The third fraction contained 0.32 g (60%) of 2-methyl-3,4-dicarbomethoxypyrrole (**3**) as a white solid: mp 162–163 °C [lit.[42] mp 159 °C]; IR (KBr) 3300, 2960, 1742, 1525, 1460, 1442, 1415, 1389, 1335, 1290, 1243, 1195, 1165, 1124, 1083, 1042, 970, 930, 810, and 770 cm^{-1}; NMR (CD_3CN, 90 MHz) δ 2.12 (s, 1 H), 2.33 (s, 3 H), 3.75 (s, 3 H), 3.77 (s, 3 H), and 7.15 (d, 1 H, J = 3 Hz); UV (95% ethanol) 260 nm (ϵ 7800) and 212 (ϵ 12 000); mass spectrum *m/e* 197 (M^+), 167, 166, 165, 149, 137, 136, 123, 111, 109, 108, 107, and 105. Anal. Calcd for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10. Found: C, 54.68; H, 5.69; N, 7.01.

Reaction of [1-(Phenylthio)ethylidene]-1-(trimethylsilyl)methylamine (1) with Acrylonitrile in the Presence of Silver Fluoride. A stirred solution containing 1.0 g of **1** and 0.53 g of acrylonitrile in 15 mL of anhydrous acetonitrile was treated with 700 mg of silver fluoride. The mixture was stirred at room temperature for 15 h and was then filtered through Celite. The filter cake was washed with methylene chloride and the combined organic extracts were removed under reduced pressure. The resulting residue was immediately dissolved in 80 mL of anhydrous benzene, and this was treated with 1.0 g of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. The mixture was stirred for 6 h at 60 °C and was then concentrated under reduced pressure. The residue was redissolved in methylene chloride and washed with a 10% sodium hydroxide solution. The organic phase was dried over magnesium sulfate and concentrated under reduced pressure to leave behind 400 mg of a thick oil which was subjected to silica gel chromatography using a 30% ethyl acetate–hexane mixture as the eluent. The major fraction contained 175 mg (39%) of a white crystalline solid whose structure was identified as 3-cyano-2-methylpyrrole (**7**) on the basis of its spectral properties: mp 131–132 °C [lit.[43] mp 133 °C]; IR (KBr) 3280, 3150, 2230, 1600, 1580, 1465, 1415, 1380, 1265, 1100, 910, 770 (s), and 750 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.41 (s, 3 H), 6.25 (t, 1 H, J = 3.0 Hz), 6.51 (t, 1 H, J = 3.0 Hz), and 9.10 (brs, 1 H); mass spectrum *m/e* 106 (M^+), 105 (base), 78, 52, and 51; UV (95% ethanol) 237 nm (ϵ 6200) and 217 (ϵ 7100). Anal. Calcd for $C_6H_6N_2$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.71; H, 5.73; N, 26.32. The other possible regioisomer (i.e., 2-methyl-4-cyano pyrrole (**10**)) was independently synthesized in order to substantiate the exclusive formation of 3-cyano-2-methylpyrrole (**7**) in this reaction.

Independent Synthesis of 2-Methyl-4-cyanopyrrole (10). A solution containing 1.0 g of (*p*-tolylsulfonyl)methyl isocyanide,[36] 0.23 g of benzyltriethylammonium chloride, and 1.42 g of methyl iodide in 20 mL of a 1:1 mixture of methylene chloride and an aqueous 30% sodium hydroxide solution was stirred at 0 °C for 3 h. At the end of this time 30 mL of water was added and the solution was extracted with methylene chloride. The combined organic layer was extracted with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 1-((methylisocyanomethyl)sulfonyl)-4-methylbenzene as a yellow oil: IR (neat) 3000, 2950, 2130, 1600, 1325, 1150, 1080, and 820 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.67 (d, 3 H, J = 7.4 Hz), 2.47 (s, 3 H), 4.70 (q, 1 H, J = 7.4 Hz), 7.43 (d, 2 H, J = 9.0 Hz), 7.88 (d, 2 H, J = 9.0 Hz). This material was used in the next step without further purification.

A suspension containing 0.78 g of potassium *tert*-butoxide in 30 mg of anhydrous tetrahydrofuran was treated dropwise with a solution of 1.0 g of the above compound and 380 mg of acrylonitrile in 8 mL of anhydrous tetrahydrofuran. The solution was stirred for 1 h, and at the end of this time water was added and the mixture was extracted with methylene chloride. The organic phase was dried over magnesium sulfate and concentrated under reduced pressure. The yellow residue was subjected to silica gel chromatography using a 20% ethyl acetate–hexane mixture as the eluent. The major fraction contained 2-methyl-4-cyanopyrrole (**10**) as a white crystalline solid: mp 61–62 °C; IR (KBr) 3280, 2235, 1595, 1530, 1465, 1425, 1140, and 820 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.23 (s, 3 H), 6.12 (m, 1 H), 7.13 (m, 1 H), and 9.47 (brs, 1 H); mass spectrum, *m/e* 106 (M^+), 105 (base), 78, 52, and 51; UV (95% ethanol) 238 nm (ϵ 4400) and 216 (ϵ 6300). Anal. Calcd for $C_6H_6N_2$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.84; H, 5.74; N, 26.31.

Reaction of [1-(Phenylthio)ethylidene]-1-(trimethylsilyl)methylamine (1) with Fumaronitrile in the Presence of Silver Fluoride. A stirred solution containing 850 mg of **1** and 425 mg of fumaronitrile in 12 mL of anhydrous acetonitrile was treated with 550 mg of silver fluoride. The mixture was stirred at room temperature for 14 h and was then filtered through Celite. The filter cake was washed with methylene chloride, and the combined organic extracts were removed under reduced pressure. Chromatography of the crude residue on neutral alumina using acetone as the eluent gave 420 mg (75%) of a white solid which was identified as 4,5-dihydro-3,4-dicyano-2-methylpyrrole (**27**) on the basis of its spectral properties: mp 73–74 °C; IR (KBr) 3330, 3280, 3150, 2230, 2180, 1595, 1505, 1470, 1460, 1425, 1390, 1305, 1265, and 1220 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.05 (s, 3 H), 3.85 (dd, 1 H, J = 10.8 and 6.6 Hz), 3.92 (dd, 1 H, J = 10.8 and 10.8 Hz), 4.04 (ddd, 1 H, J = 10.8, 6.6, and 1.0 Hz), and 5.34 (brs, 1 H). When this material was washed with deuterium oxide, the peak at δ 5.34 disappeared: mass spectrum, *m/e* 131, 130, 106, 105, 77, and 76.

A solution containing 160 mg of **27** in 15 mL of anhydrous tetrahydrofuran at 0 °C was treated with 200 mg of potassium *tert*-butoxide. The solution was warmed to room temperature and was stirred for 4 h. At the end of this time water was poured into the reaction mixture so as to decompose the excess base. The solution was then extracted with chloroform, and the organic layer was dried over magnesium sulfate. Concentration of the solution under reduced pressure gave 120 mg of 2-methyl-3-cyanopyrrole (**7**) as a white solid. This material was identical in all respects with the material isolated from the reaction of **1** with acrylonitrile in the presence of silver fluoride.

Reaction of [1-(Phenylthio)ethylidene]-1-(trimethylsilyl)methylamine (1) with Methyl Propiolate in the Presence of Silver Fluoride. A stirred solution containing 500 mg of **1** and 355 mg of methyl propiolate in 7 mL of anhydrous acetonitrile was treated with 350 mg of silver fluoride. The mixture was stirred at room temperature for 12 h and was then filtered through Celite. The filter cake was washed with methylene chloride, and the combined organic extracts were removed under reduced pressure to give a brown oil. This material was chromatographed on a silica gel column using a 10% ethyl acetate–hexane mixture as the eluent. The first and second fractions contained diphenyl disulfide and a cis–trans mixture of methyl 3-thiophenyl-2-propenoate:[35] NMR ($CDCl_3$, 90 MHz) trans isomer δ 3.81 (s, 3 H), 5.75 (d, J = 15.5 Hz), 7.83 (d, J = 15.5 Hz), and 7.2–7.6 (m, 5 H); cis isomer δ 3.81 (s, 3 H), 5.92 (d, J = 10.0 Hz), 7.29 (d, J = 10.0 Hz), and 7.2–7.6 (m, 5 H).

The third fraction contained 67 mg (23%) of 3-carbomethoxy-2-methylpyrrole (**4**) as a white crystalline solid: mp 62–63 °C [lit.[44] mp 63–64 °C]; IR (KBr) 3300, 3147, 3030, 2960, 1685, 1570, 1445, 1462, 1330, 1269, 1186, 1170, 1122, 1090, 1050, 890, 783, and 747 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.54 (s, 3 H), 3.87 (s, 3 H), 6.51 (s, 1 H), 6.54 (s, 1 H), and 9.00 (brs, 1 H); UV (95% ethanol) 255 nm (ϵ 6480) and 225 (ϵ 7260); mass spectrum, *m/e* 139 (M^+), 124, 108, 107, 106, 80, and 79.

(41) Kaydos, J. A.; Smith, D. L. *J. Org. Chem.* **1983**, *48*, 1096.
(42) Gabel, N. W. *J. Org. Chem.* **1962**, *27*, 301.
(43) Elsom, L. F.; Jones, R. A. *J. Chem. Soc. B* **1970**, 79.
(44) Anderson, M.; Johnson, A. W. *J. Chem. Soc.* **1965**, 2411.

Anal. Calcd for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.33; H, 6.47; N, 10.11.

Chemical confirmation of this structure was obtained by comparison with an independently synthesized sample prepared by the hydrogenation of *N*-benzyl-3-carbomethoxy-2-methylpyrrole (**28**).[45] A solution containing 200 mg of *N*-benzyl-3-carbomethoxy-2-methylpyrrole (**28**) and a catalytic quantity of palladium on charcoal in 50 mL of absolute ethanol was shaken on a Parr hydrogenator unit under a 60-psi atmosphere of hydrogen for 36 h. At the end of this time the solution was filtered through Celite. The filter cake was washed with methylene chloride, and the combined organic extracts were removed under reduced pressure to give 80 mg of 3-carbomethoxy-2-methylpyrrole (**4**) which was identical in all respects with the material isolated from the silver fluoride reaction.

The fourth fraction contained 98 mg (33%) of a white solid whose structure was assigned as 2-methyl-4-carbomethoxypyrrole (**5**) on the basis of its spectral properties: mp 117–118 °C [lit.[46] mp 118 °C]; IR (KBr) 3200, 2980, 2960, 1645, 1560, 1485, 1420, 1370, 1310, 1240, 1195, 1125, 1090, 1055, 980, 920, 810, and 750 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.26 (s, 3 H), 3.79 (s, 3 H), 6.29 (brs, 1 H), 7.28 (dd, 1 H, J = 2.8 and 1.6 Hz), and 8.32 (brs, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 12.6, 50.8, 107.0, 116.3, 122.3, 128.7, and 165.5; UV (95% ethanol) 260 nm (ϵ 5530) and 224 (ϵ 7950); mass spectrum, m/e 139 (M^+) 109, and 80. Anal. Calcd for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.53; H, 6.55; N, 10.03.

Chemical confirmation of this structure was obtained by comparison with an authentic sample prepared by the transesterification reaction of 2-methyl-4-carboethoxypyrrole (**29**). A solution containing 1.7 g of 2-methyl-4-carboethoxypyrrole[47] (**29**) and 10 drops of concentrated sulfuric acid in 175 mL methanol was heated at reflux for 6 days. At the end of this time the solution was diluted with water and extracted with methylene chloride. The methylene chloride layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure to give 300 mg of a brown residue. Recrystallization of this material from ethyl acetate–hexane produced a white crystalline solid whose spectral properties were identical with 2-methyl-4-carbomethoxypyrrole (**5**) obtained from the silver fluoride reaction.

Reaction of [1-(Phenylthio)ethylidene]-1-(trimethylsilyl)methylamine (1) with Benzaldehyde in the Presence of Silver Fluoride. A solution containing 500 mg of **1** and 300 mg of benzaldehyde in 7 mL of dry acetonitrile was treated with 350 mg of silver fluoride. The mixture was stirred at room temperature in the dark for 12 h and was then filtered through a Celite column. The filter cake was washed with methylene chloride and the solvent was removed under reduced pressure. Analysis of the resulting residue by NMR spectroscopy showed that it contained two major products in a 1.5:1.0 ratio. The minor product (24%) was assigned the structure of 4,5-dihydro-2-methyl-5-phenyloxazole (**31**) on the basis of its spectral properties and by comparison with an independently synthesized sample (lit.[48] bp 60 °C (0.5 mm)); IR (neat) 3075, 3040, 2945, 2880, 1960, 1885, 1820, 1680, 1610, 1498, 1455, 1440, 1390, 1310, 1290, 1224, 1270, 1182, 1082, 1045, 1030, 982, 950, 912, and 765 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.01–2.04 (m, 3 H), 3.71 (ddq, 1 H, J = 14.1, 7.9, and 1.5 Hz), 4.18 (ddq, 1 H, J = 14.1, 10.1, and 1.4 Hz), 5.41 (dd, 1 H, J = 10.1 and 7.9 Hz), 7.2–7.36 (m, 5 H); UV (95% ethanol) 257 nm (150) 250 nm (110); m/e 161 (M^+), 105, 91, and 77.

Unless oxazoline **31** was rapidly chromatographed, it was hydrolyzed to a new compound whose structure was assigned as *N*-(2-hydroxy-2-phenylethyl)acetamide (**32**) on the basis of its spectral properties: mp 122–123 °C (lit.[49] mp 124 °C); IR (KBr) 3310, 3270, 3090, 1655, 1555, 1500, 1445, 1430, 1390, 1380, 1368, 1350, 1320, 1300, 1280, 1242, 1203, 1097, 1068, 935, 840, 762, 700, and 670 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.97 (s, 3 H), 3.1–3.5 (m, 2 H), 3.69 (ddd, 1 H, J = 13.5, 8.5, and 3.5 Hz), 5.92 (br s, 1 H), 4.85 (dd, 1 H, J = 8.5 and 3.5 Hz), and 7.39 (s, 5 H). When this material was washed with deuterium oxide the following NMR spectrum was obtained: H NMR δ 1.97 (s, 3 H), 3.29 (dd, 1 H, J = 13.5 and 8.5 Hz), 3.69 (dd, 1 H, J = 13.5 and 3.5 Hz), 4.85 (dd, 1 H, J = 8.5 and 3.5 Hz), and 7.39 (s, 5 H); mass spectrum, m/e 179 (M^+), 107, 105, 79, and 77; UV (95% ethanol) 264 nm (ϵ 135), 258 (ϵ 190), 252 (ϵ 140), and 247 (ϵ 90). Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.92; H, 7.36; N, 7.77. Further chemical confirmation of the structure of this material was obtained by comparison with an independently synthesized sample prepared by the acylation of commercially available 2-amino-1-phenylethanol (**33**).

The major product (34%) isolated from the chromatotron unit was assigned the structure of 2,5-dihydro-4-methyl-5-phenyloxazole (**30**) by comparison with an independently synthesized sample: IR (neat) 3090, 3070, 3018, 2980, 2920, 2860, 1960, 1895, 1663, 1605, 1492, 1450, 1432, 1380, 1352, 1290, 1217, 1082, 1071, 1037, 1020, 955, 935, 848, 820, and 755 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 1.88–1.89 (m, 3 H), 5.44 (brdd, 1 H, J = 5.6 and 3.7 Hz), 5.59 (ddq, 1 H, J = 10.4, 3.7, and 1.5 Hz), 5.77 (ddq, 1 H, J = 10.4, 5.6, and 1.4 Hz), 7.2–7.4 (m, 5 H). External irradiation of the signal at δ 1.89 gave rise to a series of doublet of doublets at 5.44 (dd, J = 5.6 and 3.7 Hz), 5.59 (dd, J = 10.4 and 3.7 Hz), and 5.77 (dd, J = 10.4 and 5.6 Hz); UV (95% ethanol) 258 nm (ϵ 850) and 250 (ϵ 890); mass spectrum m/e 161 (M^+), 120, 119, 105, 92, 91, 90, 89, and 77.

Independent Synthesis of 2,5-Dihydro-4-methyl-5-phenyloxazole (30). A sample of 4-methyl-5-phenyloxazolidine (**35**) was prepared according to the procedure of Kalm.[50] A suspension containing 15.1 g of (+)-norephedrine (**34**) in 50 mL of water was shaken with 10 g of a 37% aqueous formaldehyde solution in a separatory funnel for 10 min. The mixture was extracted with chloroform, and the organic extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to give 4-methyl-5-phenyloxazolidine (**35**) as a white solid: mp 71–72 °C; IR (neat) 3420, 2980, 2925, 2880, 2860, 1495, 1453, 1380, 1350, 1297, 1192, 1170, 1155, 1087, 1065, 1047, 1005, 980, 918, 908, 882, 825, and 720 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.65 (d, 3 H, J = 6.7 Hz), 3.30–3.57 (m, 2 H), 4.41 (d, 1 H, J = 4.5 Hz), 4.82 (d, 1 H, J = 4.5 Hz), 4.96 (d, 1 H, J = 6.7 Hz), 7.23 (s, 5 H).

A solution containing 3.5 g of the above solid in 30 mL of benzene was cooled to 0 °C and was treated with a solution containing 2.7 g of *tert*-butyl hypochlorite in 20 mL of benzene. The mixture was stirred for 8 h at room temperature and was then treated with 2.9 g of triethylamine. The solution was heated for 12 h at 50 °C, and the triethylamine hydrochloride which had formed was filtered. Removal of the solvent under reduced pressure left an orange oil. Distillation of this material at 62 °C (0.1 mm) gave 2,5-dihydro-4-methyl-5-phenyloxazole (**30**) as a clear oil whose spectral properties were identical with a sample obtained from the reaction of [1-(phenylthio)ethylidene]-1-(trimethylsilyl)methylamine (**1**) with benzaldehyde in the presence of silver fluoride.

Independent Synthesis of 4,5-Dihydro-2-methyl-5-phenyloxazole (31). A mixture containing 1.65 g of 2-amino-1-phenylethanol (**33**) and 3.9 g of triethyl orthoacetate was heated at reflux for 2 days in the presence of a trace amount of concentrated sulfuric acid. At the end of this time the mixture was concentrated under reduced pressure, and the residue was distilled at 58 °C (0.2 mm) to give 4,5-dihydro-2-methyl-5-phenyloxazole (**31**) as a colorless oil whose spectral properties were identical with a sample obtained from the reaction of [1-(phenylthio)-ethylidene]-1-(trimethylsilyl)methylamine (**1**) with benzaldehyde in the presence of silver fluoride.

Irradiation of Diazirine in Acetonitrile in the Presence of Fumaronitrile. A solution (100 mL) containing 0.02 M diazirine and 1 M fumaronitrile in acetonitrile was irradiated for 2 h by using a Pyrex filter with a 1000-W Xe–Hg lamp at 0 °C. The solvent was removed under reduced pressure to give 110 mg of a yellow oil (92% purity). The oil was purified by VPC (5% SE-30, 180 °C) to give 2-methyl-3-cyanopyrrole (**7**) as a white solid. This material was identical in all respects with an authentic sample.

Irradiation of Diazirine in Acetonitrile in the Presence of Dimethyl Acetylenedicarboxylate. A solution (100 mL) containing 0.016 M diazirine and 0.05 M dimethyl acetylenedicarboxylate in acetonitrile was irradiated for 2 h by using a 1000-W Xe–Hg lamp ($CuSO_4$ solution filter) at 0 °C. The solvent was removed under reduced pressure to give 150 mg of a yellow oil (87% purity). This material was subjected to silica gel chromatography using ether as the eluent. The major fraction was identified as 2-methyl-3,4-dicarbomethoxypyrrole (**3**). This compound was identical in every detail with the material isolated from the reaction of **1** with dimethyl acetylenedicarboxylate in the presence of silver fluoride.

Irradiation of Diazirine in Acetonitrile in the Presence of Acrylonitrile. A solution (100 mL) containing 0.02 M diazirine and 1 M acrylonitrile in acetonitrile was irradiated for 2 h by using a Pyrex filter with a 1000-W Xe–Hg lamp at 0 °C. The solvent was removed under reduced pressure. The mixture was subjected to silica gel chromatography using a mixture of acetone–ether as the eluent. The major fraction contained 110 mg of a colorless liquid. This material was dissolved in 10 mL of benzene and was treated with 0.5 g of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. The mixture was stirred at room temperature for 12 h and was then filtered. The filtrate was subjected to silica gel chroma-

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tography using a ether-hexane mixture as the eluent. The two major fractions contained 2-methyl-3-cyanopyrrole (**7**) and 2-methyl-4-cyanopyrrole (**10**), respectively. The ratio of the two isomers (1:1) was determined by VPC analysis (5% SE-30) after DDQ oxidation. The spectral properties of the two materials were identical with authentic samples.

Irradiation of Diazirine in Acetonitrile in the Presence of Methyl Acrylate. The experimental procedure used was the same as that described for the reaction of diazirine in acetonitrile in the presence of acrylonitrile. The ratio of the two cyclic regioisomers **4** and **5** obtained after DDQ oxidation was 1:1.

Irradiation of Diazirine in Acetonitrile in the Presence of Methyl Propiolate. The experimental procedure used was the same as described for the reaction of diazirine in acetonitrile in the presence of dimethyl acetylenedicarboxylate. The ratio of the two cycloaddition products **4** and **5** was 1:1.

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Registry No. 1, 103852-58-0; **2**, 98587-57-6; **3**, 90610-59-6; **4**, 3168-85-2; **5**, 40611-76-5; **7**, 26187-27-9; **10**, 42046-60-6; **24**, 98587-59-8; **25**, 103852-60-4; *trans*-**26**, 59790-39-5; *cis*-**26**, 59790-38-4; **27**, 101402-41-9; **30**, 98587-60-1; **31**, 66614-71-9; **32**, 3306-05-6; **33**, 7568-93-6; **35**, 42794-92-3; $CH_2{=}N_2$, 334-88-3; CH_3CN, 75-05-8; diazirine, 157-22-2; (*p*-tolylsulfonyl)methyl isocyanide, 10564-55-3; 1-((methylisocyanomethyl)sulfonyl)-4-methylbenzene, 81993-07-9; maleic anhydride, 108-31-6; fumaronitrile, 764-42-1; diethyl fumarate, 623-91-6; dimethyl acetylenedicarboxylate, 762-42-5; diethyl maleate, 141-05-9; benzaldehyde, 100-52-7; acrylonitrile, 107-13-1; methyl acrylate, 96-33-3; methyl propiolate, 922-67-8; (trimethylsilyl)methyl triflate, 64035-64-9.

Polyene Cyclization Strategy in the Stereospecific Synthesis of *B/C-trans*-Morphinan. A Total Synthesis of (±)-*O*-Methylpallidinine

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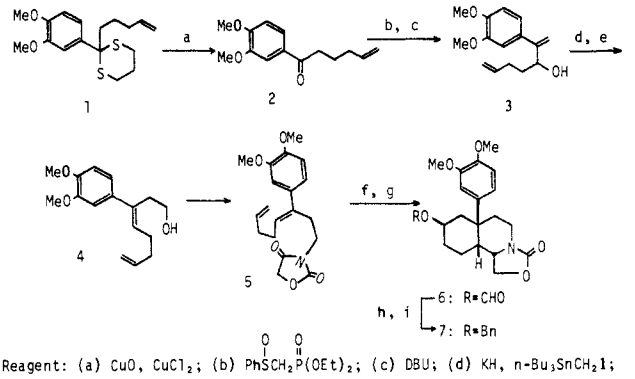
Abstract: Reduction of the oxazolidine-2,4-dione **5** with $NaBH_4$ followed by cyclization with formic acid gave the 6a-aryloxazoloisoquinolin-8-formate **6** with stereospecificity. A stereospecific synthesis of 6-hydroxy-*B/C-trans*-morphinan **15** was achieved from **5**. Oxidation of **15** yielded the 6-oxo-*B/C-trans*-morphinan **16** which constituted a formal total synthesis of (±)-*O*-methylpallidinine.

The field of biomimetic cationic polyene cyclization has been used in the synthesis of complex multicyclic compounds with excellent stereocontrol.[1,2] Polyene cyclization by the use of *N*-acyliminium ion as a cationic initiating center[3,4] has also been applied to a synthesis of some azapolycyclic systems.[5] The results[6] from our laboratory have demonstrated that *N*-acyliminium ion-induced polyene cyclization provided an efficient route to *cis*-4a-aryldecahydroisoquinolin-6-ols with stereospecificity. A-strain[7] caused by phenyl and butenyl side chains in the benzylcationic intermediates was found to be significant to control the stereochemical course of this cyclization.[6] In view of the large amount of work on a synthesis of morphine-based structural

Scheme I



Reagent: (a) CuO, $CuCl_2$; (b) $PhSCH_2P(OEt)_2$; (c) DBU; (d) KH, n-Bu_3SnCH_2I; (e) n-BuLi; (f) $NaBH_4$; (g) HCOOH; (h) NaOH; (i) $C_6H_5CH_2Br$

variants,[8] a synthesis of 6-oxygenated *B/C-trans*-morphinan derivatives has been of considerable interest from both synthetic and medicinal points of view.[9] Furthermore, 6-oxo-*B/C-trans*-morphinan can be easily convertible to B/C-cis isomer by known chemistry.[10] Our interest in a synthetic effort to create routes

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