1593, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.70–7.14 (m, 8 H), 4.60 (s, 2 H), 4.47 (br s, 2 H, varies in position between 3.0 and 5.0 ppm), 4.11 (dd, J = 8 Hz, 1 H), 3.51 (ddd, J = 9.5, 8, 8 Hz, 1 H), 3.33 (ddd J = 9.5, 7, 5 Hz, 1 H), 2.36 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 163.7, 146.4, 143.1, 128.2, 127.8, 126.4, 125.7, 125.5, 124.4, 123.9, 119.3, 118.6, 117.3, 50.2, 47.3, 43.8, 25.5; HRMS, m/z 263.1422 (calcd for $C_{17}H_{17}N_3$, m/z 263.1424).

***N,N*-Dimethyl-2-(1,2,3,9-tetrahydropyrrolo[2,1-*b*]quinazolin-3-yl)benzenamine, Vasicoline (1).** The quinazoline **12** was purified prior to use by preparative thin-layer chromatography (alumina) eluting with 60% ethyl acetate/hexane. All solvents and reagents were degassed before use by bubbling argon through the solutions for several minutes.

A 1 N ethanolic potassium hydroxide solution was generated and added (0.41 mL, 0.41 mmol) to a solution of iron pentacarbonyl (0.027 g, 0.137 mmol) in 0.16 mL of ethanol in a 10-mL round-bottomed flask fitted with a rubber septum. The system was connected with a gas bubbler and carbon monoxide was introduced and maintained at a slight positive pressure. This mixture was allowed to stir for 2 h at room temperture. Formaldehyde (0.023 g, 0.301 mmol) was then introduced, followed by addition of an ethanolic solution of the quinazoline **12** (0.036 g, 0.137 mmol). The septum was replaced with a reflux condenser, and the reaction mixture was heated at 60 °C under a slightly positive pressure of carbon monoxide for 48 h. The solution was acidified with a few drops of 3 N hydrochloric acid and concentrated to give the hydrochloride salt of **1**, which was liberated after a basic workup using ammonium hydroxide. Following extraction with ether and drying over anhydrous sodium sulfate, removal of the solvent afforded 0.041 g (99%) of **1** as a light yellow oil. Due to its extreme susceptibility toward oxidation, the product was handled under a nitrogen atmosphere at all times: IR ($CHCl_3$) 3050, 2930, 2850, 2820, 2780, 1621, 1593, 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.92–7.25 (m, 8 H), 4.70 (d, J = 10 Hz, 1 H), 4.62 (d, J = 10 Hz, 1 H), 4.54 (dd, J = 9, 8 Hz, 1 H), 3.36 (m, 2 H), 2.71 (s, 6 H), 2.35–2.60 (m, 1 H), 1.95 (ddd, J = 15, 13, 7.6, 1 H); ^{13}C NMR ($CDCl_3$) δ 164.9, 153.1, 143.6, 137.6, 128.9, 128.2, 127.6, 124.5, 123.7, 120.8, 119.3, 50.0, 47.6, 46.0 (2 C), 43.8, 29.8 (two carbons unresolved); HRMS, m/z 291.1730 (calcd for $C_{19}H_{21}N_3$, m/z 291.1737).

3-[2-(Dimethylamino)phenyl]-2,3-dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one, Vasicolinone (2). Vasicoline (0.030 g, 0.10 mmol) was allowed to stand in a solution of chloroform exposed to air for 3 days, at which point ^1H NMR indicated complete conversion to the oxidized product **2**. This compound could be chromatographed on silica, eluting with 40% ethyl acetate/hexane to afford 0.030 g of pure vasicolinone (95%): IR ($CHCl_3$) 1666, 1612, 1464, 1334 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.31 (d, J = 8 Hz, 1 H, (7.58–7.72 (m, 2 H), 7.43 (ddd, J = 8, 8, 1.8 Hz, 1 H), 7.27–7.31 (m, 2 H), 7.10–7.14 (m, 2 H), 5.04 (t, J = 9 Hz, 1 H), 4.42 (ddd, J = 13, 9, 4 Hz, 1 H), 4.15 (ddd, J = 13, 8, 8 Hz, 1 H) 2.71–2.86 (m, 1 H), 2.65 (s, 6 H), 2.24 (ddd, J = 18, 13, 9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 161.7, 161.2, 153.2, 149.5, 136.7, 133.8, 129.1, 128.4, 127.2, 126.2, 126.0, 125.0, 121.6, 120.4, 46.0 (2 C), 45.6, 45.0, 29.7; HRMS, m/z 305.1550 (calcd for $C_{19}H_{19}N_3O$, m/z 305.1530).

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Registry No. (±)-**1**, 113010-09-6; (±)-**2**, 113010-10-9; (±)-**6**, 113010-11-0; (±)-**7**, 113010-12-1; (±)-**8**, 113010-13-2; (±)-**9**, 113010-14-3; (±)-**10**, 113010-15-4; (±)-**11**, 113010-16-5; (±)-**12**, 113010-17-6.

Nucleophilic Addition to Oxazolium Salts: Stabilized Azomethine Ylides via 2-Substituted 4-Oxazolines

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Treatment of oxazolium salts with cyanide generates 4-oxazolines **2** in situ. Ring opening to azomethine ylides **3** occurs spontaneously and 2 + 3 cycloadducts are obtained in the presence of acrylate, propiolate, or acetylenedicarboxylate dipolarophiles. In the case of acetylenic dipolarophiles, loss of HCN occurs under the reaction conditions and leads directly to pyrroles **5**. The propiolate experiments are complicated by the formation of six-membered adducts **17** in some cases. This reaction pathway is explained by the addition of the acetylide anion derived from propiolate to the dipole, followed by cyclization. Sulfide nucleophiles can also be used to generate 4-oxazolines, but the yields of cycloadducts are lower.

In previous papers, we have described a versatile method for carbonyl-stabilized axomethine ylide generation from oxazolium salts by the nucleophilic addition of hydride.[1] The resulting 4-oxazolines open spontaneously to ylides provided that the C_4 position is unsubstituted, and the nitrogen substituent is a relatively compact alkyl group. A useful variant of this reaction would involve addition of nucleophiles other than hydride. As an initial step toward this goal, we chose cyanide as the attacking nucleophile due to its minimal steric demands and its potential to act as a leaving group in the product pyrrolines or pyrrolidines. Cyano-stabilized azomethine ylides have

Table I

entry	R_2	R_5	product	yield, % TMSCN/CsF	yield, % Et_4NCN
a	Ph	Ph	**5a**	80	50
b	Ph	OEt	**5b**	95	
c	Ph	Me	**5c**	57	
d	Me	Ph	**5d**	16[a]	
e	Me	OEt	**5e**	74	67
f	H	Ph	**5f**	79	59
g	H	OEt	**5g**	95	

[a] 10% recovered oxazole; low material balance may be due to competing methyl deprotonation in the dipole (see ref 1).

(1) (a) Vedejs, E.; Grissom, J. W. *J. Am. Chem. Soc.* **1986**, *108*, 6433. (b) Vedejs, E.; Grissom, J. W., submitted for publication in *J. Am. Chem. Soc.* (c) Vedejs, E.; Grissom, J. W. *J. Org. Chem.*, following paper in this issue.

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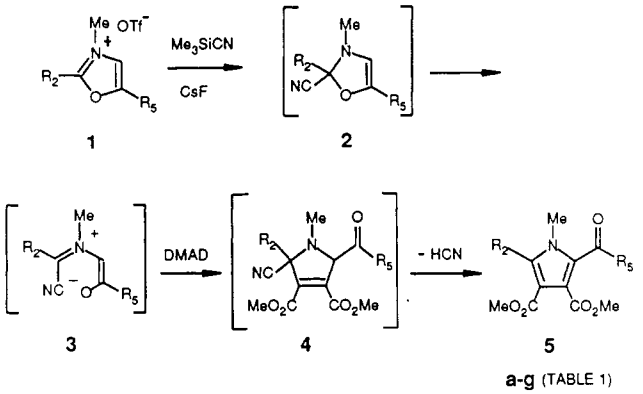

1 2 3 4 5

Figure 1.

been generated by thermolysis of cyanoaziridines[2] and cyano imines;[3] however, a systematic study of the effect of cyanide on the reactivity and regioselectivity of the dipoles has not been undertaken.

Oxazolium salts were produced by N-methylation of oxazoles with methyl triflate. As shown in Figure 1, treatment of these salts **1** with trimethylsilyl cyanide (TMSCN) + CsF/acetonitrile in the presence of dimethyl acetylenedicarboxylate (DMAD) gave the pyrroles **5**[1] in good to excellent yields. A soluble cyanide source, tetraethylammonium cyanide (NEt_4CN), also led to pyrrole products; however, the yields were lower (Table I).

A general mechanism to account for these results is presented in Figure 1. The nucleophilic cyanide anion generated in situ from TMSCN/CsF or from the soluble NEt_4CN adds to the oxazolium salt to form 2-cyano-4-oxazoline **2**. Spontaneous ring opening of the oxazoline leads to cyano acyl stabilized ylide **3**, which undergoes a [2 + 3] cycloaddition with DMAD to give the cyano-3-pyrroline **4**. This intermediate is never observed since it immediately loses HCN to afford the product pyrrole **5**. The HCN loss probably proceeds via nitrogen lone pair assisted expulsion of cyanide followed by deprotonation to yield the pyrrole. The rapid dehydrocyanation of cyanopyrrolines has been observed previously in cyanoaziridine thermolysis/DMAD addition.[2a]

As discussed in our earlier report, oxazolines which are substituted by alkyl or aryl groups in both the C_4 and C_5 positions do not readily form azomethine ylides.[1] Instead, the oxazolines undergo a [2 + 2] addition to form an unusual bicyclic oxazoline structure. When 1,2,4,5-tetramethyloxazolium salt was treated with TMSCN/CsF in the presence of DMAD, no identifiable products were obtained. The absence of any compounds resulting from [2 + 2] addition between the cyanooxazoline and DMAD suggests that the basicity of the oxazoline enamine moiety is moderated by the inductive effect of the α-cyano group.

The acyl cyano azomethine ylides can also undergo cycloadditions with olefinic acceptors such as methyl acrylate (Figure 2),[4] but the results can be quite complex due to the formation of regioisomers and stereoisomers. In a relatively well behaved example, the salt derived from 2-methyl-5-ethoxyoxazole (**6e**) was treated with TMSCN/CsF in the presence of methyl acrylate to yield the unstable pyrrolidine **7**. Pyrrolidine **7** readily lost HCN

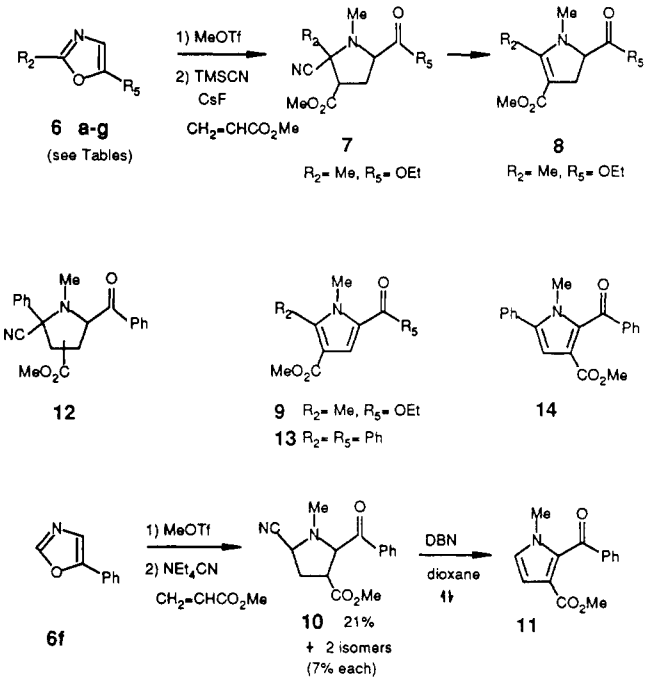

Figure 2.

Table II

entry	R_2	R_5	R	yield, % 15	16	17
a	Ph	Ph	Et	10		54
b	Ph	OEt	Et	61	12	
c	Ph	Me	Et	17		28
d	Me	Ph	Et	*d*	*d*	*d*
e	Me	OEt	Et	61	28	
f[a,c]	H	Ph	Et	55	*b*	
g	H	OEt	Me	89		

[a] This reaction was carried out with NEt_4CN as the cyanide source. [b] 23% of an unidentified pyrrole which has lost benzoyl but retained cyanide was isolated. [c] When the reaction was carried out with TMSCN/CsF, the yield of **15f** was 27%, and 33% of the unknown pyrrole was isolated. [d] No adducts observed.

to give pyrroline **8** in 73% yield. Subsequent DDQ oxidation led to pyrrole **9**. The regiochemistry was established by comparison to an authentic sample.[1]

In a more complex example, application of this method to 5-phenyloxazole (**6f**) resulted in the isolation of three adducts of which cyanopyrrolidine **10** was the major product (21%). The two minor products (7% each) were isomeric adducts of unknown regiochemistry. The regiochemical assignment of **10** was made by conversion to the known pyrrole **11**.[1] The pyrrolidine **10** and the two isomeric adducts are the only stable cyano azomethine ylide [2 + 3] adducts in the entire series, and their stability appears to be related to the lack of an additional substituent at the cyanide-bearing carbon.[4] The regiochemistry of the major product from oxazole **6f** is reversed compared to what is seen with oxazole **6e**, but the ratio is not clear since the minor products could not be unambiguously identified.

Addition of cyanide to 1-methyl-2,5-diphenyloxazolium salt in the presence of methyl acrylate led to a complex mixture of isomeric cyanopyrrolidines and -pyrrolines **12**. However, upon heating this mixture in refluxing toluene in the presence of DDQ, the two pyrroles **13** and **14** were obtained in 56% and 7% yields, respectively. The ratio of regioisomers in the initial addition step can be inferred from the ratio of pyrroles, but the stereochemistry is not clear.

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(4) For previous examples, see: Texier, F.; Guenzet, J.; Merah, B. *C. R. Hebd. Seances Acad. Sci., Ser. C.* **1973**, *277*, 1371.

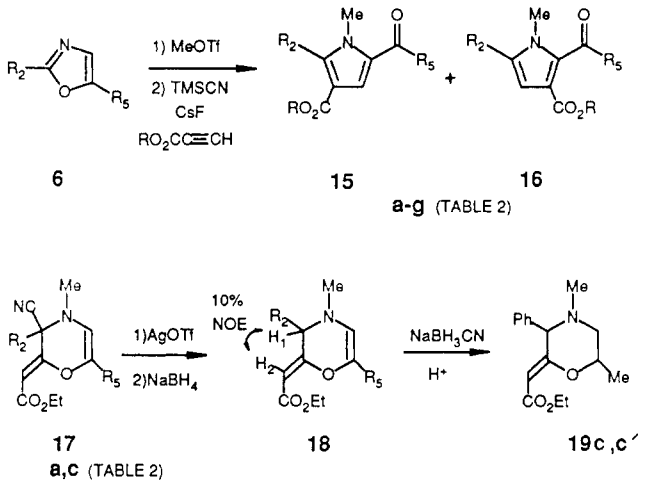

Figure 3.

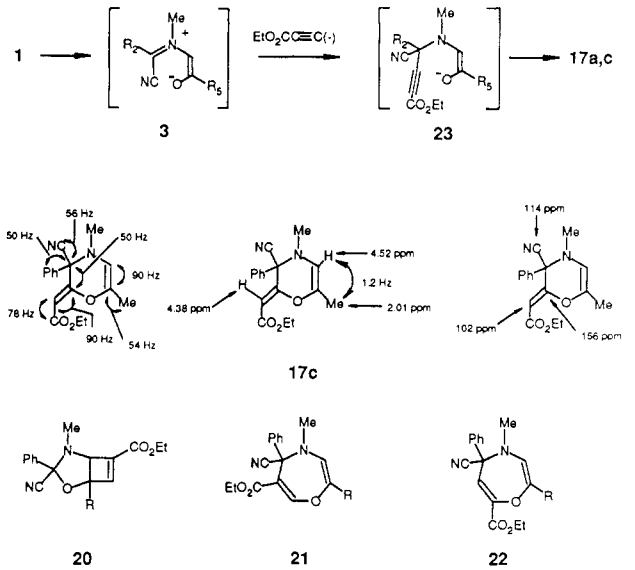

Figure 4.

Due to the instability and difficulty in characterizing the intermediate cyanopyrrolidines in the methyl acrylate trapping experiments, regiochemical issues were probed further using propiolate as the acceptor. As summarized in Table II, alkylation of 2-phenyl-5-ethoxyoxazole (**6b**) followed by cyanide addition in the presence of propiolate led to a mixture of pyrroles in which **15b** was the predominant regioisomer (61%, Figure 3). Application of this procedure to 5-ethoxyoxazole (**6g**) gave an 89% yield of pyrrole **15g**, while the analogous reaction of 2-methyl-5-ethoxyoxazole (**6e**) produced both of the pyrroles **15e** (61%) and **16e** (28%). These examples represent cyano ester stabilized azomethine ylides which appear to be relatively well behaved. The situation with the cyano acyl stabilized ylides is not so straightforward.

As typical examples, 2,5-diphenyloxazole (**6a**) and 2-phenyl-5-methyloxazole (**6c**) each gave a single [2 + 3] pyrrole adduct in low yield; the regiochemistry observed corresponds to the major product seen in the cyano ester propiolate additions. However, the major product in each of these two examples was an anomalous six-membered adduct, **17a** from **6a** and **17c** from **6c**. The C_2-unsubstituted starting material, 5-phenyloxazole (**6f**) yielded 55% of the pyrrole **15f** and 23% of an unidentified pyrrole which had retained cyanide but lost benzoyl. Application of this procedure to 2-methyl-5-phenyloxazole (**6d**) gave no adducts at all.

Support for the unusual cyanodihydrooxazine structures **17a** and **17c** comes from spectral and chemical considerations (Figure 3 and 4). Mass spectra of both compounds include a strong molecular ion that supports a 1:1 adduct which has not lost cyanide. The cyanide cannot be detected in the IR spectrum, but this is not surprising since the presence of an α-heteroatom often weakens the intensity of the CN stretching frequency considerably.[5] The proton NMR spectrum of **17c** has a 1.2-Hz coupling between the vinylic proton and the vinyl methyl group. No other coupling is seen, suggesting the isolation of this unit between the oxygen and nitrogen. The same connectivity is also present in the precursor 4-oxazoline. The other vinyl proton comes at 4.58 ppm in **17a** and 4.38 ppm in **17c**; the strong shielding effect is presumably caused partly by the phenyl group α to nitrogen, and partly by the donor effect of the vinyl ether (vinylogous carbonate) oxygen.

Evidence for the cyanide location α to nitrogen comes from its reductive removal (Ag^+; $NaBH_4$). Thus, both **17a** and **17c** can be reduced to the hydrolytically unstable dihydrooxazines **18a** and **18c**, respectively. The proton α to nitrogen (H_1) and the vinyl proton α to ester (H_2) in **18a** are somewhat broadened and exhibit a mutual 10% NOE enhancement. The instability of these compounds probably derives from the sensitivity of the enamine functionality. By comparison, the α-cyano group inductively stabilizes the analogous starting enamines to the point where compounds **17a** and **17c** are stable for months. The presence of the enamine structure in **17c** and **18c** could be confirmed by trifluoroacetic acid/$NaCNBH_3$ reduction to the tetrahydrooxazine **19**.[6] Compounds **17a** and **18a** did not reduce under these conditions, presumably due to unfavorable conformational and steric factors.

The strongest support for structures **17a** and **17c** comes from the ^{13}C NMR data. The ^{13}C resonances of **17a** show the presence of cyanide (114 ppm), a vinylogous carbonate (102 ppm doublet and 156 ppm singlet), and most importantly, the obvious lack of a benzoyl group (no signals below 164 ppm). All chemical shift and C–H coupling information is consistent with the proposed structures. The carbon–carbon connectivity of **17c** could be derived from the high-resolution C–H decoupled ^{13}C NMR spectrum by measurement of the coupling constants between carbon satellites. In particular, the upfield olefinic carbon on the vinylogous carbonate (101 ppm) is coupled both to the ester carbon (164.4 ppm, 78 Hz) and to the other carbon of the vinylogous carbonate (156.0 ppm, 90 Hz).

Other structures that were considered but discounted on the basis of the spectral evidence were bicyclic oxazolidine **20**, corresponding to [2 + 2] addition between the propiolate and the cyano-4-oxazoline, and the unusual heterocycles **21** and **22**, analogous to the [2 + 5] cycloaddition betwen *N*-acyl azomethine ylides and DMAD reported by Nozaki et al.[7] Structure **20** was ruled out because it fails to adequately account for the ^{13}C signals at 101 (doublet) and 156 ppm (singlet). Structures **21** and **22** were discarded because the vinylogous carbonate carbon at 156 ppm (in **17c**) is not coupled to the ester carbon (164 ppm).

A rationale to explain the formation of the observed products which is consistent with the experimental evi-

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dence is presented in Figure 4. Cyanide adds to the oxazolium salt **1** to form the cyanooxazoline **2** which opens to the cyano acyl stabilized azomethine ylide **3**. The ylide can undergo the expected [2 + 3] cycloaddition with propiolate, followed by loss of HCN to generate pyrrole **15**. However, there is a competing pathway leading to the cyanodihydrooxazine. This involves nucleophilic attack at the iminium carbon of dipole **3** by the sterically undemanding propiolate anion, generated in low concentration by the basic cyanide. The resulting enolate **23** can undergo internal Michael addition to yield the observed product **17** after proton transfer. The observation that a large excess of propiolate favors oxazine formation is consistent with this explanation if the amount of oxazine formed reflects the amount of acetylide anion which is available.

The differing behavior of the ester cyano and keto cyano stabilized azomethine ylides in the propiolate additions probably reflects their differing relative reactivity in the [2 + 3] cycloaddition. In frontier molecular orbital terms[8] the reaction of an azomethine ylide with an electron deficient dipolarophile is suggested to be a dipole HOMO controlled reaction.[9] Thus, the dominant FMO involves the HOMO of the dipole and the LUMO of the dipolarophile, and factors that decrease the HOMO–LUMO gap should increase the efficiency of the reaction. Generally, donor and/or conjugator groups (alkyl, alkoxy, aryl) on the dipole raise the HOMO energy, while acceptor groups on the dipolarophile lower the LUMO energy. This combination of effects facilitates the reaction. However, in the case of stabilized azomethine ylides, the dipole contains electron-deficient groups (cyano, ester, benzoyl, or acetyl) which tend to lower the HOMO and moderate the dipole reactivity. These stabilized dipoles are reactive enough to participate in cycloadditions with highly electron-deficient dipolarophiles such as acrylate, DMAD, and maleimide. The presence of cyanide in addition to an ester or acyl electron-withdrawing group in **3** further decreases dipole reactivity and allows time for the anomalous side reaction to occur in the most highly deactivated cyano acyl dipoles.

In an attempt to increase the dipole reactivity in the acyl-stabilized dipoles, the trimethylsilyl cyanide reagent was replaced by trimethylsilyl ethyl sulfide in the initial oxazolium addition step. This change would replace the acceptor cyanide substituent by the donor thioethyl group in the dipole **3**. The reaction of the salt **1d** derived from 2-methyl-5-phenyloxazole with trimethylsilyl ether sulfide/CsF utilizing DMAD as the trapping agent yielded 25% of the pyrrole **5d** compared with 16% obtained in the cyanide addition. However, when this procedure was applied to 2,5-diphenyloxazole, the yield of **5a** was 28%, far below the 80% observed when using cyanide as the activator. In the addition of the ethylthio anion to 2-phenyl-5-methyloxazole in the presence of propiolate, the yield of pyrrole **15c** was 10%. No products analogous to the oxazine structures were observed, suggesting that acetylide ion formation had not occurred. In view of the poor yields this approach was not pursued further.

Cyanide benzoyl stabilized dipole **3f** (R_2 = H, R_5 = Ph) behaves differently compared to the other cyano acyl stabilized dipoles. By use of a soluble cyanide source, the yield of pyrrole **15f** is 55%. There is no evidence for the cyanodihydrooxazine **17** which is observed with the cyano keto ylides **3a** and **3d**, even though sterically the addition of propiolate anion should be more favorable in this case. Apparently the [2 + 3] cycloaddition benefits even more from reduced steric hindrance.

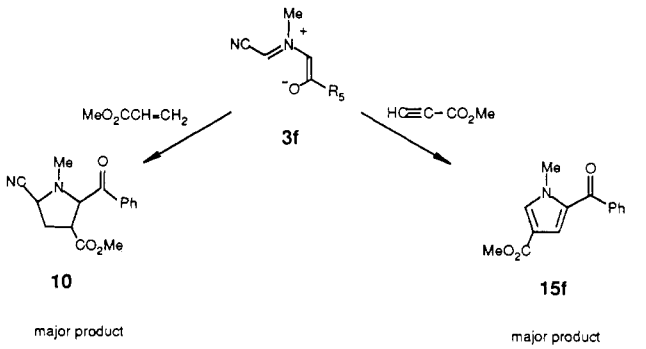

Figure 5.

Examination of the regiochemistry observed from propiolate and acrylate trapping of azomethine ylides **3** raises questions regarding the directive influence of the cyano substituent. Analogous trapping of ylides having H in place of the CN group usually gives products having the acyl-substituted ylide carbon attached to the β-dipolarophile carbon.[1,11] Surprisingly, the same regiochemistry preference is seen with the CN-containing ylides **3** even though the directing effect of cyanide should oppose that of the acyl group. In FMO terms, the largest coefficient on the dipole apparently resides on the carbon substituted by the acyl group[8,10,11] since the polarization of the dipolarophile is well-known.[8] Presumably, cyanide does not greatly affect the orbital polarization that is already present in the carbonyl-stabilized dipoles.

The most unusual examples are those where the dipole **3** is substituted by cyanide at one end and a benzoyl group at the other (Figure 5). "Normal" propiolate addition regiochemistry is seen with the dipole **3f** substituted by benzoyl at one terminus and cyanide at the other, and the favored product is **15f**. However, the major product **10** from the corresponding acrylate addition is formed with the opposite regiochemistry. In an earlier study, we noted that a benzoyl-substituted dipole corresponding to **3f**, but having H in place of CN, reacts with the "abnormal" regiochemistry with both acrylate and propiolate while the ester-stabilized dipole behaves normally.[1] The origins of these anomalies are not clear, and reactions of the benzoyl-stabilized dipoles are unpredictable and substrate dependent. Although frontier molecular orbital theory can help to correlate the overall trends, we have been unable to explain the anomalous examples without resorting to unproved assumptions.

The cyanide oxazolium procedure is a useful method for the conversion of oxazoles into pyrroles with the incor-

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poration of two carbons from an acetylenic dipolarophile. The method is not as general as the phenylsilane reductive activation technique,[1] but pyrroles are formed directly without the need for a DDQ oxidation step.

Experimental Section

Proton nuclear magnetic resonance (NMR) spectra were obtained on a Bruker WP200 200 MHz, WP270 270 MHz or AM500 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) relative to solvent peak ($CDCl_3$ 7.24 ppm, CD_3CN 1.93 ppm, and acetone-d_6 2.09 ppm). Infrared spectra (IR) were recorded with a Beckman Acculab 7 or a Mattson FT IR spectrometer and calibrated with a polystyrene peak (1601.8 cm^{-1}). Mass spectra were obtained on an MS-80 high-resolution mass spectrometer. Melting points were obtained on a hot stage microscope apparatus and are not corrected.

Column chromatagraphy was performed with Kieselgel 60 flash silica gel. Solvents were dried as follows: diethyl ether (Et_2O), dioxane, tetrahydrofuran (THF), and glyme (dimethoxyethane) were distilled from sodium/benzophenone; halocarbons and hydrocarbons were distilled from calcium hydride; hexane and EtOAc for silica gel chromatography were flash distilled prior to use; acetonitrile was distilled first from CaH_2 then from P_2O_5. All reagents that are not referenced were obtained from Aldrich. All 2-substituted 5-alkoxyoxazoles were made by the method of Cornforth.[12] Other oxazoles were made by the following literature procedures: 2-methyl-5-phenyloxazole,[13] 2-phenyl-5-methyloxazole,[13] 5-phenyloxazole,[14] 5-ethoxyoxazole.[15]

Anhydrous reactions were carried out under a N_2 atmosphere. Anhydrous cesium fluoride was prepared by flame-drying under vacuum, taking care not to fuse the salt.

Trimethylsilyl Cyanide/CsF Addition to Oxazolium Salts: DMAD-Trapping Products. Table I, Figure 1 Results. Pyrroles 5a–g. General Experimental Procedure. Methyl triflate (0.028 mL, 0.249 mmol) was added to a solution of the oxazole (0.226 mmol) in 2 mL of acetonitrile. After the mixture was stirred for 2 h at room temperature, TMSCN (0.060 mL, 0.452 mmol) and dimethyl acetylenedicarboxylate (DMAD, 0.139 mL, 1.13 mmol) were added and the mixture transferred by cannula to anhydrous cesium fluoride (0.069 g, 0.452 mmol) in acetonitrile (4 mL). After being stirred overnight, the reaction mixture was poured into 20 mL of EtOAc and washed with dilute KOH. The organic layer was dried ($MgSO_4$) and the solvent evaporated to leave a dark brown residue, which was purified by silica gel chromatography to yield the pyrrole **5**. All pyrroles were identical with those prepared from the phenylsilane reduction/DDQ oxidation of oxazolium salts using DMAD as a trap.[1] The individual details in each case are as follows.

1. **Entry a. Pyrrole 5a**: 0.068 g, 0.181 mmol, 80%.
2. **Entry b. Pyrrole 5b**: 0.074 g, 0.215 mmol, 95%.
3. **Entry c. Pyrrole 5c**: 0.041 g, 0.128 mmol, 57%.
4. **Entry d. Pyrrole 5d**: 0.011 g, 0.036 mmol, 16%.
5. **Entry e. Pyrrole 5e**: 0.047 g, 0.167 mmol, 74%.
6. **Entry f. Pyrrole 5f**: 0.054 g, 0.178 mmol, 79%.
7. **Entry g. Pyrrole 5g**: 0.058 g, 0.214 mmol, 95%; solid, mp 82–86 °C (hexane); MS, m/e, exact mass calcd for $C_{12}H_{15}O_6N$ 269.0895, found 269.0861, error 12.7 ppm; IR (CH_2Cl_2, cm^{-1}) C=O (1760, C=O 1750, C=O 1710; 270-MHz NMR ($CDCl_3$, ppm) 7.27 (1 H, s), 4.23 (2 H, q, J = 7.1 Hz), 3.89 (3 H, s), 3.88 (3 H, s), 3.75 (3 H, s), 1.28 (3 H, t, J = 7.1 Hz).

Tetraethylammonium Cyanide Addition to Oxazolium Salts: DMAD-Trapping Products. Table I Results. Pyrroles 5a, 5e, and 5f. General Experimental Procedure. Methyl triflate (0.028 mL, 0.249 mmol) was added to a solution of the oxazole (0.226 mmol) in 2 mL of acetonitrile. After the mixture was stirred for 2 h at room temperature, DMAD (0.139 mL, 1.13 mmol) and 2 mL of acetonitrile were added to the reaction flask. NEt_4CN[16] (0.071 g, 0.452 mmol) in 2 mL of acetonitrile was added dropwise over a 20-min period. After being stirred overnight, the reaction mixture was poured into 20 mL of EtOAc and washed with dilute KOH. The organic layer was dried ($MgSO_4$) and the solvent evaporated to leave a dark brown residue, which was purified by silica gel chromatography to yield the pyrrole **5**.

1. **Entry a. Pyrrole 5a**: 0.043 g, 0.113 mmol, 50%.
2. **Entry e. Pyrrole 5e**: 0.043 g, 0.151 mmol, 67%.
3. **Entry f. Pyrrole 5f**: 0.046 g, 0.151 mmol, 59%.

Trimethylsilyl Cyanide/CsF Addition to Oxazolium Salts: Methyl Acrylate Trapping Products 7–14. Figure 2 Results. General Experimental Procedure. The reactions were carried out as described above for the DMAD/TMSCN additions except that methyl acrylate (0.102 mL, 1.13 mmol) was used as the trap. After the reaction was stirred overnight, the solvent was removed and the residue eluted through a silica gel plug by using 5:4 hexane/EtOAc to remove base line impurities. The resultant oils were characterized as described below.

1,2-Methyl-5-ethoxyoxazole 6e. A crude NMR spectrum of the resulting oil showed the cyanated pyrrolidine **7**. Silica gel chromatography yielded the pyrroline **8** as a clear oil (0.036 g, 0.160 mmol, 71%). The oil was dissolved in 2 mL of dioxane, DDQ (0.038 g, 0.168 mmol) was added, and the solution was refluxed 12 h. The reaction mixture was poured into 20 mL of EtOAc and washed with 1 N KOH (3 × 20 mL). The organic layer was dried ($MgSO_4$) and the solvent evaporated under reduced pressure to leave pyrrole **9**, which was identical with the pyrrole prepared from the phenylsilane reduction/DDQ oxidation of the oxazolium salt using methyl propiolate as a trap.

Pyrrolidine 7: unstable product, not isolable; formula, $C_{12}H_{18}O_4N_2$; 270-MHz NMR ($CDCl_3$, ppm) 4.22–4.08 (2 H, m), 3.73 (3 H, s), 3.27 (1 H, dd, J = 10.3, 5.1 Hz), 3.00 (1 H, t, J = 9.5 Hz), 2.71–2.48 (1 H, m), 2.40 (3 H, s), 2.25–2.16 (1 H, m), 1.62 (3 H, s), 1.23 (3 H, t, J = 7.1 Hz).

Pyrroline 8: oil; flash silica gel Kieselgel 60, 5:4 hexane/EtOAc, R_f 0.3; MS, m/e, exact mass calcd for $C_{11}H_{17}O_4N$ 227.1153, found 227.1161, error 3.6 ppm; IR (CH_2Cl_2, cm^{-1}) C=O 1740, C=O 1680, other 1605; 270-MHz NMR ($CDCl_3$, ppm) 4.22–4.08 (2 H, m), 4.01 (1 H, dd, J = 12.7, 8.3 Hz), 3.58 (3 H, s), 3.08–2.91 (1 H, m), 2.77 (3 H, s), 2.73–2.67 (1 H, m), 2.18 (3 H, s), 1.23 (3 H, t, J = 7.1 Hz).

Pyrrole 9: solid, mp 67–69 °C (hexane); MS, m/e, exact mass calcd for $C_{11}H_{15}O_4N$ 225.0997, found 225.0998, error 0.4 ppm; IR (CH_2Cl_2, cm^{-1}) C=O 1690, C=O 1712; 270-MHz NMR ($CDCl_3$, ppm) 7.31 (1 H, s), 4.24 (2 H, q, J = 7.1 Hz), 3.82 (3 H, s), 3.77 (3 H, s), 2.52 (3 H, s), 1.31 (3 H, t, J = 7.1 Hz).

2. 5-Phenyloxazole (6f). The crude oil was chromatographed to yield pyrrolidine **10** (0.025 g, 0.092 nmol, 21%) and two isomeric adducts of unknown regiochemistry in a 1:1 mixture n(0.016 g, 0.062 mmol, 14%). Pyrrolidine **10** was dissolved in dioxane, and a drop of DBN was added. The reaction was refluxed overnight to yield a 1:1 mixture of the pyrrole **11** and an unidentified product. The pyrrole **11** was identical with the pyrrole prepared from the phenylsilane reduction/DDQ oxidatio nof this oxazolium salt using methyl propiolate as a trap.[1]

Pyrrolidine 10: oil; flash silica gel Kieselgel 60, 5:4 hexane/EtOAc, R_f 0.27; MS, m/e, exact mass calcd for $C_{15}H_{16}O_3N_2$ 272.1157, found 272.1143, error 5.2 ppm; IR (CH_2Cl_2, cm^{-1}) C=O 1745, C=O 1684; 270-MHz NMR ($CDCl_3$, ppm) 8.07–7.90 (2 H, m), 7.65–7.42 (3 H, m), 4.77 (1 H, d, J = 5.6 Hz), 4.19 (1 H, dd, J = 5.2, 5.2 Hz), 3.69 (3 H, s), 3.18 (1 H, q, J = 8.3 Hz), 2.64–2.56 (2 H, m), 2.50 (3 H, s). ^{13}C NMR ($CDCl_3$, ppm) 198.2 (s), 172.1 (s), 135.6 (s), 134.0 (d), 128.8 (d), 128.5 (d), 117.4 (s), 68.4 (d), 54.9 (q), 52.7 (d), 46.8 (d), 36.7 (t), 32.0 (q).

Pyrrole 11: oil, analytical TLC (silica gel F254), 5:4 hexane/EtOAc, R_f 0.65; MS, m/e, no peak match parent, formula $C_{14}H_{13}O_3N$; IR (CH_2Cl_2, cm^{-1}) C=O 1712, C=O 1640; 270-MHz NMR ($CDCl_3$, ppm) 7.82–7.70 (2 H, m), 7.58–7.42 (3 H, m), 6.57 (1 H, d, J = 3.1 Hz), 6.48 (1 H, d, J = 3.1 Hz), 3.80 (3 H, s), 3.59 (3 H, s).

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Two unidentified isomeric adducts of 10: oil, analytical TLC (silica gel F254), 5:4 hexane/EtOAc, R_f 0.26; MS, *m/e*, no peak match, parent, M - 27, 245.1052, calcd 245.1042, error 4 ppm; formula $C_{15}H_{16}O_3N_2$; IR ($CHCl_3$, cm^{-1}) C=O 1750, C=O 1690; 270-MHz NMR ($CDCl_3$, ppm) 8.00–7.88 (2 H, m), 7.65–7.42 (3 H, m), 4.56 (0.5 H, d, J = 9 Hz), 4.38 (0.5 H, d, J = 6.7 Hz), 4.25 (0.5 H, dd, J = 11.1, 6.7 Hz); 4.18 (0.5 H, dd, J = 9.0, 2.0 Hz), 3.78 (1.5 H, s), 3.54–3.42 (1 H, m), 3.29 (1.5 H, s), 2.97–2.74 (1 H, 7), 2.52 (1.5 H, s), 2.49 (1.5 H, s), 2.48–2.40 (0.5 H, m); 2.14 (0.5 H, ddd, J = 13.8, 9.0, 6.3 Hz).

3. 2,5-Diphenyloxazole (6a). The crude NMR spectrum of the resultant oil **12** showed a complex mixture of regio- and stereoisomers. The oil was dissolved in 2 mL of toluene, DDQ (0.056 g, 0.248 mmol) was added, and the reaction was refluxed 12 h. The reaction mixture was poured into 20 mL of EtOAc and washed with 1 N KOH (3 × 20 mL). The organic layer was dried ($MgSO_4$) and the solvent evaporated under reduced pressure to leave a yellow oil. Purification on a silica gel column (5:2 hexane/EtOAc) gave pyrroles **13** (0.040 g, 0.126 mmol, 56%) and **14** (0.005 g, 0.015 mmol, 7%). These pyrroles were identical with those synthesized by using the phenyl silane reduction/DDQ oxidation using DMAD as a trap.[1]

Pyrrole 13: oil; flash silica gel Kieselgel 60, 5:4 hexane/EtOAc, R_f 0.5; MS, *m/e*: exact mass calcd for $C_{20}H_{17}O_3N$ 319.1204, found 319.119, error 4.5 ppm; IR ($CDCl_3$, cm^{-1}) C=O 1710, C=O 1695; 270-MHz NMR ($CDCl_3$, ppm) 7.91–7.84 (2 H, m), 7.62–7.36 (8 H, m), 7.26 (1 H, s), 3.79 (3 H, s), 3.63 (3 H, s).

Pyrrole 14: oil; flash silica gel Kieselgel 60, 5:4 hexane/EtOAc, R_f 0.5; MS, *m/e*, exact mass calcd for $C_{20}H_{17}O_3N$ 319.1204, found 319.119, error 4.5 ppm; IR ($CDCl_3$, cm^{-1}) C=O 1710, C=O 1695; 270-MHz NMR ($CDCl_3$, ppm) 7.91–7.84 (2 H, m), 7.62–7.36 (8 H, m), 6.67 (1 H, s), 3.66 (3 H, s), 3.31 (3 H, s).

Trimethylsilyl Cyanide/CsF Addition to Oxazolium Salts: Propiolate-Trapping Products. Figure 3, Table II Results. Pyrroles 15 and 16. General Experimental Procedure. The procedure was carried out as described above for the DMAD/TMSCN reactions except that propiolate (methyl or ethyl, 1.13 mmol) was used as the trap. Purification of the reaction products by silica gel chromatography yielded the pyrroles **15** and/or **16**. All pyrroles **15** and **16** were identical with pyrroles prepared from the phenylsilane reduction/DDQ oxidation using propiolate as a trap.[1]

1. Entry b. Pyrrole 15b: 0.042 g, 0.137 mmol, 61%.

Pyrrole 16b: 0.008 g, 0.027 mmol, 12%.

2. Entry e. Pyrrole 15e: 0.034 g, 0.142 mmol, 63%.

Pyrrole 16e: 0.015 g, 0.063 mmol, 28%.

3. Entry g. Pyrrole 15g: 0.042 g, 0.201 mmol, 89%.

Trimethylsilyl Cyanide/CsF Addition to 2,5-Diphenyl-3-methyloxazolium Salt in the Presence of Propiolate: Table II Results. Pyrrole 15a and Oxazine 17a. Methyl triflate (0.028 mL, 0.249 mmol) was added to a solution of the oxazole (0.050 g, 0.226 mmol) in 2 mL of acetonitrile. After the mixture was stirred for 2 h at room temperature, TMSCN (0.060 mL, 0.452 mmol) and ethyl propiolate (0.113 mL, 1.13 mmol) were added, and the mixture was transferred by cannula to anhydrous cesium fluoride (0.069 g, 0.452 mmol) in acetonitrile (4 mL). After being stirred overnight, the reaction mixture was poured into 20 mL of EtOAc and washed with dilute KOH. The organic layer was dried ($MgSO_4$) and the solvent evaporated to leave a dark brown residue, which was purified by silica gel chromatography (10:1 hexane/EtOAc) to yield the pyrrole **15a**, the oxazine **17a**, and ethyl β-cyanoacrylate.[17] The pyrrole **15a** was identical with the pyrrole prepared from the phenylsilane reduction/DDQ oxidation protocol using propiolate as a trap.[1]

Pyrrole 15a: 0.008 g, 0.023 mmol, 10%.

Cyanodihydrooxazine 17a: 0.044g, 0.122 mmol, 54%; solid, mp 126–130 °C (hexane/EtOAc); MS, *m/e*, exact mass calcd for $C_{22}H_{20}O_3N_2$ 360.1469, found 360.1478, error 2.5 ppm; IR (CH_2Cl_2, cm^{-1}) C=O 1730; 270-MHz NMR ($CDCl_3$, ppm) 7.73–7.59 (4 H, m), 7.56–7.47 (3 H, m), 7.43–7.32 (2 H, m), 7.28–7.20 (1 H, m), 6.32 (1 H, s), 4.58 (1 H, s), 4.20 (2 H, q, J = 7.1 Hz), 2.56 (3 H, s), 1.28 (3 H, t, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$ (DEPT), ppm) 164.0 (s), 156.1 (s), 134.8 (s), 133.3 (s), 131.6 (s), 130.2 (d), 129.4 (d), 128.4 (d), 128.2 (d), 127.2 (d), 122.7 (d), 114.3 (d), 114.3 (s), 102.1 (d), 64.1 (s), 60.3 (t), 39.1 (q), 14.3 (q).

Trimethylsilyl Cyanide/CsF Addition to 2-Phenyl-3,5-dimethyloxazolium Salt in the Presence of Propiolate: Table II Results. Pyrrole 15c and Oxazine 17c. The reaction procedure was followed as described above except that 2-phenyl-3,5-dimethyloxazolium salt was used. The resulting dark brown residue was purified by HPLC (10:1 hexane/EtOAc) to yield the pyrrole **15c**, the oxazine **17c**, and ethyl <<b-cyanoacrylate. The pyrrole **15c** was identical with the pyrrole prepared from the phenylsilane reduction/DDQ oxidation protocol using propiolate as a trap.[1]

Pyrrole 15c: 0.010 g, 0.038 mmol, 17%.

Cyanodihydrooxazine 17c: 0.019 g, 0.063 mmol, 28%; oil, analytical TLC (silica gel F254), 5:1 hexane/EtOAc; MS, *m/e*, exact mass calcd for $C_{17}H_{18}O_3N_2$ 298.1313, found 298.1317, error 1.4 ppm; IR (CH_2Cl_2, cm^{-1}) C=O 1735; 270-MHz NMR ($CDCl_3$, ppm) 7.58–7.51 (2 H, m), 7.47–7.41 (3 H, m), 5.42 (1 H, d, J = 1.0 Hz), 4.38 (1 H, s), 4.14–4.02 (2 H, m), 2.32 (3 H, s), 2.01 (3 H, d, J = 1.0 Hz), 1.19 (3 H, t, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$ (DEPT), ppm) 164.4 (s), 156.0 (s), 133.5 (s), 133.4 (s), 130.0 (d), 129.2 (d), 128.2 (d), 114.0 (s), 113.9 (d), 101.0 (d), 64.5 (s), 59.9 (t), 38.7 (q), 15.9 (q), 13.9 (q).

Trimethylsilyl Cyanide/CsF Addition to 3-Methyl-5-phenyloxazolium Salt in the Presence of Propiolate: Table II Results. Pyrrole 15f and Unidentified Pyrrole. The procedure was repeated as described above except that 3-methyl-5-phenyloxazolium salt was used. The resulting dark brown residue was purified by silica gel chromatography to yield the pyrrole **15f**, an unidentified pyrrole, and ethyl β-cyanoacrylate. The pyrrole **15f** was identical with the pyrrole prepared from the phenylsilane reduction/DDQ oxidation protocol using propiolate as a trap.[1]

Pyrrole 15f: 0.016 g, 0.061 mmol, 27%.

Unidentified pyrrole: 0.013 g, 0.074 mmol, 33%; solid, mp 78–80 °C (hexane/EtOAc); MS, *m/e*, exact mass calcd for $C_9H_{10}O_2N_2$ 178.074, found 178.0743, error 1.6 ppm; IR (CH_2Cl_2, cm^{-1}) C=O 1715, CN 2213; 200-MHz NMR ($CDCl_3$, ppm) 7.36 (1 H, d, J = 0.8 Hz), 7.17 (1 H, d, J = 0.8 Hz), 4.26 (2 H, q, J = 7.0 Hz), 3.80 (3 H, s), 1.31 (3 H, t, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$ (DEPT), ppm) 162.7 (s), 130.9 (d), 120.8 (d), 117.2 (s), 112.3 (s), 105.3 (s), 60.3 (t), 35.8 (q), 14.3 (q).

Reduction of Cyanodihydrooxazine 17a to Dihydrooxazine 18a: Figure 3 Results. Cyanodihydrooxazine **17a** (0.209 g, 0.580 mmol) was dissolved in CH_2Cl_2 (10 mL), and AgOTf (0.164 g, 0.638 mmol) was added. The reaction was stirred at room temperature 1 h, at which time the reaction was filtered through a plut of glass wool to remove the AgCN precipitate. Removal of the solvent under reduced pressure left the iminium salt, which was dissolved in anhydrous ethanol (10 mL). $NaBH_4$ was added, and stirring was commenced for 1 h, at which time the reaction mixture was poured into $CHCl_3$ (20 mL) and washed with H_2O (2 × 20 mL). The organic layer was dried (K_2CO_3) and the solvent removed under reduced pressure to leave the moderately unstable dihydrooxazine **18a** (0.183 g, 0.545 mmol, 94%).

18a: oil, analytical TLC (silica gel F254), 5:4 hexane/EtOAc, R_f 0.76; MS, *m/e*, no peak match, parent, formula $C_{21}H_{21}O_3N$; 200-MHz NMR ($CDCl_3$, ppm) 7.65–7.53 (2 H, m), 7.50–7.08 (8 H, m), 6.31 (1 H, s), 4.91 (1 H, s), 4.44 (1 H, s), 4.18 (2 H, q, J = 7.0 Hz), 2.69 (3 H, s), 1.28 (3 H, t, J = 7.0 Hz).

Reduction of Cyanodihydrooxazine 17c to Dihydrooxazine 18c: Figure 3 Results. Cyanodihydrooxazine **17c** (0.084 g, 0.282 mmol) was dissolved in CH_2Cl_2 (5 mL) and AgOTf (0.072 g, 0.282 mmol) added. The reaction was stirred at room temperature 1 h, at which time the reaction was filtered through a plug of glass wool to remove the AgCN precipitate. Removal of theesolvent under reduced pressure left the iminium salt, which was dissolved in anhydrous ethanol (5 mL). $NaBH_4$ was added, and stirring was commenced for 1 h, at which time the reaction mixture was poured into $CHCl_3$ (10 mL) and washed with H_2O (2 × 10 mL). The organic layer was dried (K_2CO_3) and the solvent removed under reduced pressure to leave the unstable dihydrooxazine **18c**, which was not purified further.

18c: sample unstable to chromatography; R_f 0.76, 5:4 hexane/EtOAc on silica gel; MS, *m/e*, no peak match parent, formula $C_{16}H_{19}O_3N$; 270-MHz NMR ($CDCl_3$, ppm) 7.35–7.21 (5 H, m), 5.35

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(1 H, br q, J = 1.2 Hz), 4.70 (1 H, s), 4.15 (1 H, s), 4.10 (2 H, q, J = 7.1 Hz),2.43 (3 H, s), 1.88 (3 H, d, J = 1.2 Hz), 1.22 (3 H, t J = 7.1 Hz); ^{13}C NMR ($CDCl_3$ (DEPT), ppm) 165.2 (s), 159.3 (s), 137.2 (s), 133.1 (s), 128.4 (d), 128.0 (d), 127.9 (d), 114.2 (d), 97.1 (d), 63.7 (d), 59.4 (t), 41.7 (q), 16.1 (q), 14.2 (q).

Trifluoroacetic Acid/$NaCNBH_3$ Reduction of Dihydrooxazine 18c to Dihydrooxazine 19c and 19c′:[6] Figure 3 Results. Dihydrooxazine **18c** (0.036 g, 0.132 mmol) was dissolved in MeOH (2 mL). Bromocresol green was added until a blue color was retained. Trifluoroacetic acid (2 N, MeOH) was added dropwise until the solution turned yellow. $NaCNBH_3$ (0.009 g, 0.145 mmol) was added and the reaction stirred 2 h at room temperature. Trifluoroacetic acid (2 N) was added periodically as needed to maintain a yellow color. The reaction was pounred into $CHCl_3$ (10 mL) and washed with 1 N KOH (2 × 10 mL) and the organic layer dried (K_2CO_3). The solvent was removed under reduced pressure to leave oxazine **19c** as a mixture of two diastereomers, which were separated by silica gel chromatography using 5:4 hexane/EtOAc.

19c: 0.007 g, 0.025 mmol, 19%; oil, analytical TLC (silica gel F254), 5:2 hexane/EtOAc, R_f 0.12; MS, m/e, exact mass calcd for $C_{16}H_{21}O_3N$ 275.1516, found 275.1519, error 1 ppm; IR ($CHCl_3$, cm^{-1}) C=C 1620, C=O 1710; 200-MHz NMR ($CDCl_3$, ppm) 7.36 (5 H, br s), 4.62–4.55 (1 H, m), 4.53 (1 H, d, J = 1.5 Hz), 4.13–3.96 (2 H, m), 3.80 (1 H, d, J = 1.5 Hz), 2.82 (1 H, dd, J = 12.6, 5.0 Hz), 2.68 (1 H, dd, J = 12.6, 3.5 Hz), 2.10 (3 H, s), 1.51 (3 H, d, J = 6.5 Hz), 1.16 (3 H, t, J = 7.1 Hz).

19c′: 0.011 g, 0.039 mmol, 30%; oil, analytical TLC (silica gel F254), 5:2 hexane/EtOAc, R_f 0.17; MS, m/e, exact mass calcd for $C_{16}H_{21}O_3N$ 275.1516, found 275.152, error 1.4 ppm; IR ($CHCl_3$, cm^{-1}) C=O 1700, C=C 1630; 200-MHz NMR ($CDCl_3$, ppm) 7.36 (5 H, br s), 4.37 (1 H, d, J = 1.5 Hz), 4.32–4.31 (1 H, m), 4.10–3.98 (2 H, m), 3.61 (1 H, br d, J = 1.5 Hz), 2.97 (1 H, dd, J = 12.0, 2.6 Hz), 2.33 (1 H, dd, J = 12.0, 10.9 Hz), 2.02 (3 H, s), 1.39 (3 H, d, J = 6.2 Hz), 1.17 (3 H, t, J = 7.0 Hz).

Trimethylsilyl Ethyl Sulfide/CsF Addition to Oxazolium Salts: DMAD-Trapping Products 5a and 5d. General Experimental Procedure. Methyl triflate (0.028 mL, 0.249 mmol) was added to a solution of the oxazole (0.226 mmol) in 2 mL of acetonitrile. After the mixture was stirred for 2 h at room temperature, trimethylsilyl ethyl sulfide[18] (0.070 mL, 0.452 mmol) and DMAD (0.139 mL, 1.13 mmol) were added, and the mixture was transferred by cannula to anhydrous cesium fluoride (0.069 g, 0.452 mmol) in acetonitrile (4 mL). The mixture was stirred overnight, the solvent was removed under reduced pressure and the crude residue purified on a silica gel column to yield the pyrrole.

1. 2,5-Diphenyl-oxazole (6a). Pyrrole 5a: 0.024 g, 0.063 mmol, 28%.

2. 2-Methyl-5-phenyloxazole (6d). Pyrrole 5d: 0.018 g, 0.057 mmol, 25%.

Trimethylsilyl Ethyl Sulfide Addition to 2-Phenyl-5-methyloxazole: Ethyl Propiolate Trapping. Pyrrole 15c. The procedure was carried out as described above except that ethyl propiolate (0.116 mL, 0.113 mmol) was used as the trap. After the mixture was stirred overnight, the solvent was removed under reduced pressure and the crude residue purified on a silica gel column to yield **pyrrole 15c**: 0.006 g, 0.023 mmol, 10%.

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Registry No. 5a, 102537-10-0; **5b**, 102537-12-2; **5c**, 102537-11-1; **5d**, 102537-14-4; **5e**, 102537-13-3; **5f**, 113379-75-2; **5g**, 113379-76-3; **6a**, 92-71-7; **6b**, 25755-93-5; **6c**, 5221-67-0; **6d**, 3969-09-3; **6e**, 32595-70-3; **6f**, 1006-68-4; **6g**, 15031-12-6; **7**, 113379-77-4; **8**, 113379-78-5; **9**, 113379-79-6; **10**, 113379-80-9; **11**, 11403-28-4; **13**, 113379-81-0; **14**, 113379-82-1; **15a**, 113379-83-2; **15b**, 113379-84-3; **15c**, 113379-85-4; **15e**, 113379-86-5; **15f**, 113379-87-6; **15g**, 113379-88-7; **16b**, 113379-89-8; **16e**, 68384-84-9; **17a**, 113403-29-5; **17c**, 113379-90-1; **18a**, 113379-91-2; **18c**, 113379-92-3; **19c**, 113379-93-4; **19c′**, 113379-94-5; DMAD, 762-42-5; H_2C=$CHCO_2Me$, 96-33-3; HC≡CCO_2Me, 922-67-8; HC≡CCO_2Et, 623-47-2; HC(CN)=$CHCO_2Et$, 18228-28-9; 1-methyl-2(or 5)-cyano-3-(ethoxycarbonyl)pyrrole, 113379-97-8; 2-phenyl-3,5-dimethyloxazolium salt, 113379-95-6; 3-methyl-5-phenyloxazolium salt, 113379-96-7.

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A Comparison of 4-Oxazoline and 2-Acylaziridine Routes to Azomethine Ylides

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Pyrolysis of aziridines **6** or **7** affords azomethine ylides, which can also be generated from 3-methyl-2,5-diphenyl-4-oxazoline (**1a**) at room temperature. Attempts to trap the thermally generated ylide with dimethyl acetylenedicarboxylate afford increasing amounts of the unusual enamine product **9** as the temperature decreases. The aziridine-derived dipoles (**2a** or **3a** vs **4a** or **5a**) cannot be trapped prior to equilibration. Similar results are obtained from the aziridines **16**/**17**, but in this case, dipole isomers can be intercepted by *N*-phenylmaleimide in xylene solution. The 2,3-dimethyl-5-methoxy-4-oxazoline derived dipole **2b** probably does not equilibrate, but its 2 + 3 cycloadducts correspond to the major products formed by aziridine pyrolysis under equilibrating conditions.

We have recently described a versatile method for generation of stabilized azomethine ylides from the controlled reduction of *N*-methyloxazolium salts.[1] The intermediate 4-oxazolines **1** open spontaneously to the ylides **2** (Figure 1), which can be trapped in 2 + 3 cycloaddition reactions.

Trapping of the intuitively predicted S-dipole geometry **2** was eventually confirmed on the basis of the X-ray structure determination of an acrylate adduct.[2] However, the crystalline adduct was obtained relatively late in the study, and a variety of other stereochemical correlations

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