Reaction of *N*-Allylaniline with CO/H_2, 1, and dppb. A mixture of 0.532 g (4.0 mmol) of *N*-allylaniline, 0.022 g (0.04 mmol) of 1, 0.042 g (0.10 mmol) of dppb, and 10 mL of CH_2Cl_2 was heated with stirring for 12 h at 80 °C under 48 atm of 1:1 CO/H_2. The solvent was removed by rotary evaporation, and the residue was chromatographed on silica gel using 19:1 hexane–ethyl acetate as the eluant. The yield of pure 1-phenylpyrrolidine was 0.401 g (68%). This method was also applied to *N*-allyl-*o*-anisidine, *N*-allyl-*o*-toluidine, and *N*-allyl-1-naphthylamine affording the pyrrolidines **3**,[18,19] in 55%, 63%, and 59% yields, respectively.

Reaction of *N*-Allylaniline with CO/H_2 and (dppb)Rh(COD)$^+BF_4^-$. The previous procedure was used, except for substitution of both 1 and dppb by 0.030 g of (dppb)Rh(COD)$^+BF_4^-$. In this manner, 1-phenylpyrrolidine was isolated in 75% yield.

Reaction of *N*-Allylaniline with CO/H_2, $[CODRhCl]_2$, and dppb. The reaction and workup procedure using 1 as the catalyst was applied, with substitution of 1 by 0.013 g of $[CODRhCl]_2$. 1-Phenylpyrrolidine was obtained in 69% yield.

Acknowledgment. We are indebted to British Petroleum and to the Natural Sciences and Engineering Research Council of Canada for support of this research.

Registry No. 1, 31974-01-3; **2** (Ar = Ph), 589-09-3; **2** (Ar = *p*-$CH_3OC_6H_4$), 71954-46-6; **2** (Ar = 1-$C_{10}H_7$), 22950-23-8; **2** (Ar = *o*-$CH_3OC_6H_4$), 15258-47-6; **2** (Ar = *o*-$CH_3C_6H_4$), 15316-91-3; **3** (Ar = Ph), 4096-21-3; **3** (Ar = *p*-$CH_3OC_6H_4$), 54660-04-7; **3** (Ar = 1-$C_{10}H_7$), 82238-92-4; **4** (Ar = Ph), 139944-54-0; **4** (Ar = *p*-$CH_3OC_6H_4$), 139944-55-1; **5** (Ar = Ph), 622-80-0; **5** (Ar = 1-$C_{10}H_7$), 607-60-3; **5** (Ar = *o*-$CH_3OC_6H_4$), 139944-56-2; **5** (Ar = *o*-$CH_3C_6H_4$), 83627-55-8; **6** (Ar = Ph, R = CH_3), 22774-81-8; **6** (Ar = *p*-$CH_3OC_6H_4$, R = CH_3), 139944-57-3; **6** (Ar = *o*-$CH_3OC_6H_4$, R = CH_3), 139944-58-4; **6** (Ar = *o*-$CH_3C_6H_4$, R = CH_3), 131001-34-8; **6** (Ar = *p*-ClC_6H_4, R = CH_3), 22774-84-1; **6** (Ar = 1-$C_{10}H_7$, R = CH_3), 22774-87-4; **6** (Ar = Ph, R = *n*-C_5H_{11}), 139944-59-5; **6** (Ar = 2-C_5H_4N, R = CH_3), 139944-60-8; **6** (Ar = Ph, R = CH_2SO_2Ph), 139944-61-9; **7** (Ar = Ph, R = CH_3), 106027-38-7; **7** (Ar = *p*-$CH_3OC_6H_4$, R = CH_3), 139944-62-0; **7** (Ar = *o*-$CH_3OC_6H_4$, R = CH_3), 139944-63-1; **7** (Ar = *o*-$CH_3C_6H_4$, R = CH_3), 139944-64-2; **7** (Ar = *p*-ClC_6H_4, R = CH_3), 139944-65-3; **7** (Ar = 1-$C_{10}H_7$, R = CH_3), 139944-66-4; **7** (Ar = Ph, R = *n*-C_5H_{11}), 139944-67-5; **7** (Ar = 2-C_5H_4N, R = CH_3), 139944-68-6; **8** (R = C_6H_{11}, R′ = H), 6628-00-8; **8** (R = C_6H_{11}, R′ = CH_3), 55611-45-5; **8** (R = $PhCH_2$, R′ = H), 4383-22-6; **8** (R = *n*-C_4H_9, R′ = H), 4538-09-4; **8** (R = C_8H_{15}, R′ = H), 17630-23-8; **8** (R = $PhCH_2$, R′ = CH_3), 52853-55-1; **8** (R = $PhCH_2CH_2$, R′ = H), 5263-58-1; **8** (R = CH_2=$CHCH_2$, R′ = H), 124-02-7; **9** (R = C_6H_{11}, R′ = H), 6837-24-7; **9** (R = C_6H_{11}, R′ = CH_3), 96240-05-0; **9** (R = $PhCH_2$, R′ = H), 5291-77-0; **9** (R = *n*-C_4H_9, R′ = H), 3470-98-2; **9** (R = C_8H_{15}, R′ = H), 139944-69-7; **9** (R = $PhCH_2$, R′ = CH_3), 96240-04-9; **9** (R = $PhCH_2CH_2$, R′ = H), 10135-23-6; **9** (R = CH_2=$CHCH_2$, R′ = H), 2687-97-0; $PhNHCH_2CH$=$C(CH_3)_2$, 27125-60-6; $PhNH(CH_2)_2CH(CH_3)_2$, 2051-84-5; $PhCH_2NHCH_2CH$=$CHCH_3$, 4393-07-1; $HRh(CO)(PPh_3)_3$, 17185-29-4; $RuCl_2(PPh_3)_3$, 15529-49-4; $Ru_3(CO)_{12}$, 15243-33-1; $PdCl_2(PPh_3)_2$, 13965-03-2; $NiCl_2$(dppp), 15629-92-2; *N*-isobutyl-*o*-toluidine, 139944-70-0; dichlorotricarbonylruthenium dimer, 22594-69-0; 3-methyl-1-phenylmethylpyrrolidin-2-one, 108303-99-7.

Supplementary Material Available: Spectral data for new allylic amines (2 pages). Ordering information is given on any current masthead page.

(18) Shapiro, S. L.; Freedman, L.; Soloway, H. U.S. Pat. 3,270,024; *Chem. Abstr.* **1966**, *66*, 18675v.
(19) Rozeboom, M. D.; Houk, K. N.; Searles, S.; Seyedrezai, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3448.

Synthesis of Oxazoles from *O*-Trimethylsilyl Acyltrimethylsilane Cyanohydrins

Robert F. Cunico* and Chia P. Kuan

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Received December 26, 1991

Sequential addition of organolithium reagents and acyl chlorides (or anhydrides) to *O*-trimethylsilyl acyltrimethylsilane cyanohydrins affords β-(acyloxy)-*N*,*N*-bis(trimethylsilyl) enamines which cyclize to substituted oxazoles under thermolysis or treatment with trimethylsilyl trifluoromethanesulfonate. Oxazoles were prepared containing alkyl and phenyl substituents at C-5, alkyl, alkenyl, and phenyl substituents at C-4, and alkyl, alkenyl, phenyl, and functionalized substituents at C-2.

The oxazole ring[1] serves as nucleus to a host of compounds which, depending on attendant substitution, are physiologically active,[2] serve as luminescent materials,[3] or may be employed in synthetic methodology.[4] We have reported briefly on a new approach to oxazole assemblage which suggested that substantial control could be exercised over the choice of each ring substituent.[5] Details of this process are presented here, and extension is made to additional examples in order to better define the scope of the method.

Scheme I outlines the synthetic procedure and illustrates the entry methodologies which were explored. The targeted common intermediate was the lithium β-bis(tri-

(1) Reviews: (a) Turchi, I. J., Ed. *Oxazoles*; Wiley: New York, 1986. (b) Boyd, G. V. *Comp. Heterocycl. Chem.*, Vol. 6, Pergamon: Oxford, 1984. (c) Turchi, I. J. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 32. (d) Tarent'ev, P. B.; Lomakina, N. P. *Chem. Heterocycl. Compd.* **1976**, 579. (e) Turchi, I. J.; Dewar, M. J. S. *Chem. Rev.* **1975**, *75*, 389. (f) Lakhan, R.; Ternai, B. *Adv. Heterocycl. Chem.* **1974**, *17*, 99.
(2) Recent examples are given by (a) Fusetani, N.; Sugawara, T.; Matsunaga, S. *J. Am. Chem. Soc.* **1991**, *113*, 7811. (b) Kobayashi, J.; Itagaki, F.; Shigemori, H.; Ishibashi, M.; Takahashi, K.; Ogura, M.; Nagasawa, S.; Nakamura, T.; Hirota, H.; Ohta, T.; Nozoe, S. *J. Am. Chem. Soc.* **1991**, *113*, 7812.
(3) Krasovitskii, B. M.; Bolotin, B. M. *Organic Luminescent Materials*; VCH: Weinheim, 1988.
(4) (a) Boger, D. L. *Chem. Rev.* **1986**, *86*, 781. (b) Lipshutz, B. H. *Ibid.* **1986**, 795. (c) Wasserman, H. H.; McCarthy, K. E.; Prowse, K. S. *Ibid.* **1986**, 845. (d) Dondoni, A.; Fogagnolo, M.; Mastellari, A.; Pedrini, P.; Ugozzoli, F. *Tetrahedron Lett.* **1986**, *27*, 3915. (e) Hassner, A.; Fischer, B. *J. Org. Chem.* **1991**, *56*, 3419.
(5) Cunico, R. F.; Kuan, C. P. *Tetrahedron Lett.* **1990**, *31*, 1945.

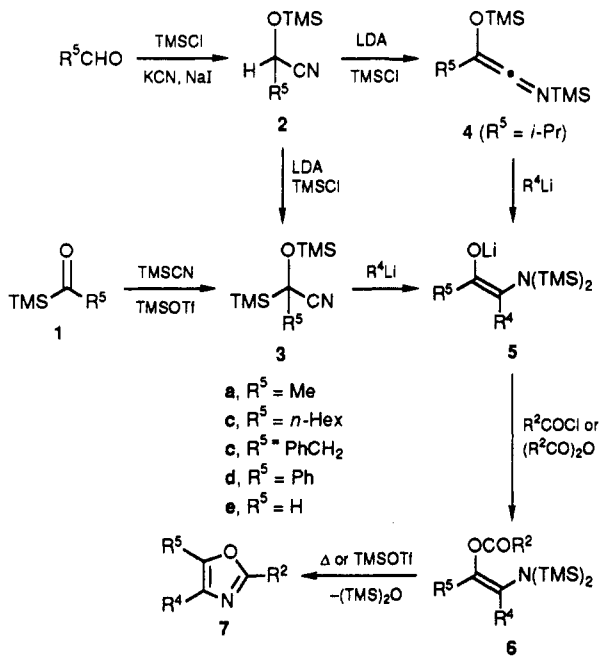
0022-3263/92/1957-3331$03.00/0

Table I. Synthesis of Acyloxy Enamines 6 and Oxazoles 7

R^2	R^4	R^5	6	yield (%)[a]	7	yield (%)[a]	method[b]
Me	Me	Me	**a**	90	**a**	95	A
t-Bu	Me	Me	**b**	78	**b**	90	C
Ph	Me	Me	**c**	73	**c**	75	C
CH=CHMe	Me	Me	**d**	78	**d**	94	A
CH_2Cl	Me	Me	**e**	44	**e**	95	A
CF_3	Me	Me	**f**	66	**f**	95	A
CO_2Et	Me	Me	**g**	84	**g**	88	B
COMe	Me	Me	**h**	*c*	**h**	62[d]	B
H	*n*-Bu	Me	**i**	*c*	**i**	73[d]	C′
OEt	Me	Me	**j**	62	**j**	55	B
Me	*t*-Bu	Me	**k**	61	**k**	93	A
Me	CH_2Ph	Me	**l**	53	**l**	84	A
Me	$CH_2CH=CH_2$	Me	**m**	58	**m**	68	C′
Me	CH_2TMS	Me	**n**	55	**n**	47[d]	A
Me	$CH=CH_2$	Me	**o**	60	**o**	92	A
Me	$C(TMS)=CH_2$	Me	**p**	84	**p**	73	C′
Me	c-C_3H_5	Me	**q**	82	**q**	45[d]	C′
Me	Ph	Me	**r**	60	**r**	95	A
Me	Me	*n*-Hex	**s**	*c*	**s**	66[d]	C′
Me	Me	*i*-Pr	**t**	76	**t**	69	C′
Me	Me	CH_2Ph	**u**	*c*	**u**	70[d]	C′
Me	Me	Ph	**v**	42	**v**	62[d]	C
Me	*n*-Bu	H	**w**	*c*	**w**	73[d]	C′
Ph	Me	Ph	**x**	30	**x**	48[d]	C
CF_3	Me	Ph	**y**	*c*	**y**	37[d]	C
Me	$N(i\text{-}Pr)_2$	*i*-Pr	**z**	*c*	**z**	49[d]	C′
(2,2′-bis)	Me	Me	**aa**	85	**aa**	46	C
1,4-C_6H_4	Me	Me	**bb**	85	**bb**	48	C

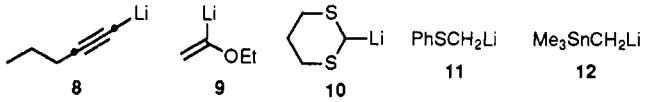
[a] Yields corrected for residual impurities as determined by VPC analysis. [b] A, FVP; B, static thermolysis; C, TMSOTf in $CHCl_3$; C′, TMSOTf in CH_2Cl_2. [c] Not isolated. [d] Overall yield from **3**.

Scheme I



methylsilyl)amino enolate **5**, which has been shown[6] to originate from sequential 1,3 (C,N) and 1,4 (O,N) silyl group migrations following the addition of organolithium reagents to the nitrile functionality of **3**. Although the preparation of *O*-trimethylsilyl cyanohydrins[7] **3** from acylsilanes[8] **1** is expected to be general, we have only employed acetyltrimethylsilane (**1**, R^5 = Me) for this purpose,[5] as we wished to explore the feasibility of obtaining **3** from the readily-available[9] *O*-trimethylsilyl cyanohydrins of aldehydes. Thus, other examples of **3** (and **4**, R^5 = i-Pr) used in this investigation were prepared by the metalation–silylation of **2**, as reported.[10]

Exploratory runs to determine the efficacy of R^4Li addition were carried out using **3a**, followed by derivatization with acetic anhydride. A variety of alkyl- and alkenyllithiums, as well as phenyllithium, were successfully employed (Table I). However, none of the organolithiums **8–12** afforded adducts,[11] and our efforts to introduce latent



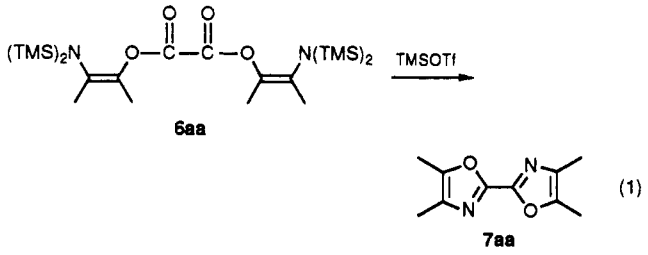
functionality directly attached to the oxazole ring at C-4 by these protocols were frustrated. As the ketenimine **4** is the principal product from the metalation–silylation of **2** (R^5 = *i*-Pr),[10] the addition of methyllithium to its C=NTMS functionality was explored.[12] This proceeded readily[13] and afforded a 76% yield of the corresponding **6** after acetylation. However, the use of **8** or **9** with **4** again afforded no significant amount of **6**. Interestingly, **4** does

(6) Cunico, R. F.; Kuan, C. P. *J. Org. Chem.* **1990**, *55*, 4634.
(7) Method of Noyori, R.; Murata, S.; Suzuki, M. *Tetrahedron* **1981**, *37*, 3899.
(8) Reviews: (a) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647. (b) Page, P. C. B., Klair, S. S., Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147.
(9) Duboudin, F.; Cazeau, Ph.; Moulines, F.; Laporte, O. *Synthesis* **1982**, 212. In our hands, the time necessary for complete preformation of TMSCN by this method was at least 2 d. An anhydrous workup (as for the preparation of **6**; see Experimental Section) was found to give **2** uncontaminated by cyanohydrin hydrolysis product.
(10) Cunico, R. F.; Kuan, C. P. *J. Org. Chem.* **1992**, *57*, 1202.
(11) By using **3a** (OTMS = $OSiMe_2$-*t*-Bu) with **10** and **11**, it was determined that removal of the C-2 TMS group of the cyanohydrin occurred in lieu of addition. The reagents **8–12** were employed in THF. Since, in general, RLi additions of **3** were found to be superior in ether, **10** and **11** were also tried in this solvent, but to no avail.
(12) *N*-TMS imines of nonenolizable aldehydes add RLi reagents: Hart, D. J.; Kanai, K.; Thomas, D. G.; Yang, T. K. *J. Org. Chem.* **1983**, *48*, 289.
(13) Qualitatively, **4** was found to be more reactive than **3**. A solution of **4** treated with MeLi at −78 °C lost its characteristic orange color upon warming to −40 °C. In contrast, neither **3a** nor **3d** was noticably reactive towards MeLi at 0 °C (15 min).

add LDA to the imine moiety,[10,14] and the intermediate **5** [$R^4 = N(i\text{-}Pr)_2$] may be acetylated to the corresponding **6**.

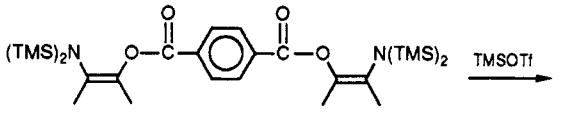
In general, acylation of **5** to **6** could be accomplished using either acid chlorides or acid anhydrides at 0–25 °C. However, pyruvyl chloride and diacid chlorides (oxalyl chloride, terephthaloyl chloride) necessitated addition at −78 °C to achieve useful yields.[15] Only one stereoisomer of each **6** was obtained, and they are represented as having *Z* stereochemistry based solely on extrapolation from analogous chemistry.[6,10] Although these **6** were hydrolytically labile, purification by distillation or chromatography on Florisil[16] was generally possible. However, pure **6** was not mandatory for subsequent cyclization and, on occasion, crude **6** was employed to obtain **7** in good overall yields (Table I).

With few exceptions, cyclization of **6** to **7** could be effected by either flash vacuum pyrolysis (FVP) at 625 °C (1 mmHg) or by trimethylsilyl trifluoromethanesulfonate (TMSOTf) treatment at 25 °C. Flash vacuum pyrolysis generally afforded higher yields of cleaner products than TMSOTf reactions, but the latter allows the method to accommodate **6** of high molecular weight. For example, the bis(enamines) **6aa** and **6bb** could be cyclized with TMSOTf to the oxazoles **7aa** and **7bb** (eqs 1 and 2). As

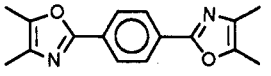


6aa

7aa (1)



6bb



7bb (2)

a direct comparison of the two approaches, FVP of **6a** afforded 95% of **7a** containing only hexamethyldisiloxane as coproduct, while TMSOTf treatment (25 °C, 3 days, $CHCl_3$)[17] gave a 77% yield of **7a** containing hexamethyldisiloxane and small amounts of several other unidentified impurities. Several exceptions to the general procedures involved **6g** and **6h**, which were found to be quite thermally labile[18] and therefore could be cyclized by static thermolysis (125 °C; 60 °C), and **6j**, which decomposed under either FVP or TMSOTf conditions but could be converted to **7j** at 140 °C. Table II summarizes the characterization data obtained for **6** and **7**.

A number of oxazole types made more accessible by the current method may be of special interest. The 4-aminooxazole **7z** appears to be the first known member of this class,[1a] and the cycloaddition reactions of 2-alkoxy-4,5-dialkyloxazoles are under investigation by others.[19] 2-Ketooxazoles such as **7h** are already known as important synthetic intermediates, and their availability is limited.[19,20] The potential to prepare 2-(chloroalkyl)-4,5-dialkyloxazoles (e.g., **7e**) may be unique to this method[21] and should afford elaborated structures via subsequent nucleophilic substitutions.

Experimental Section

NMR spectra were obtained using $CDCl_3$ solutions ($CHCl_3$ taken as δ 7.24). IR spectra were obtained on neat films. VPC analyses utilized a 4 ft × 0.25 in. 20% SE-30 column. Samples for combustion analysis were obtained by preparative VPC or from column chromatography (70–230-mesh silica gel 60 or 100-mesh Florisil). Kugelrohr distillations reflect oven temperatures and are listed as "Kd °C (mmHg)". All reactions were carried out under positive argon pressure. THF and ether were distilled from sodium benzophenone ketyl immediately before use. *n*-Butyllithium (*n*-BuLi) in hexane, *tert*-butyllithium (*t*-BuLi) in pentane, and methyllithium (MeLi) in ether were obtained from Aldrich Chemical Co.

General Method for the Preparation of β-Acyloxy Enamines 6. Between 1.0 and 3.0 mmol of **3** in ether (10 mL/mmol of **3**) was treated with 1.1 equiv of organolithium reagent (at 25 °C for MeLi, 0 °C for *n*-BuLi, −78 °C for *t*-BuLi) and the mixture was allowed to stir at 25 °C overnight (12–20 h). Then 1.1 equiv of acid chloride or acid anhydride was added (at 0 °C unless indicated otherwise) and the mixture was held at 25 °C for an additional 2–3 h. An anhydrous workup was then carried out by removing volatiles under vacuum (25 °C, 1 mm), adding pentane, and filtering the suspension through Celite (glass frit) under Ar. Kugelrohr distillation (Kd) or column chromatography on Florisil (hexane to 5% ether–hexane) followed.

2-[Bis(trimethylsilyl)amino]-3-(ethanoyloxy)-2-butene (6a). From **3a**, MeLi, and acetyl chloride. Kd 40–45 °C (2 mm); over 95% pure.

2-[Bis(trimethylsilyl)amino]-3-[(2,2-dimethylpropanoyl)oxy]-2-butene (6b).[5]

2-[Bis(trimethylsilyl)amino]-3-(benzoyloxy)-2-butene (6c). From **3a**, MeLi, and benzoyl chloride. Kd 65–70 °C (0.8 mm); over 95% pure.

2-[Bis(trimethylsilyl)amino]-3-((*E*)-2-propenoyloxy)-2-butene (6d). From **3a**, MeLi, and (*E*)-2-propenoyl chloride. Kd 65–70 °C (4 mm); over 90% pure.

2-[Bis(trimethylsilyl)amino]-3-[(chloroethanoyl)oxy]-2-butene (6e). From **3a**, MeLi, and chloroethanoyl chloride. Kd 50–55 °C (2 mm); 80% pure.

2-[Bis(trimethylsilyl)amino]-3-[(trifluoroethanoyl)oxy]-2-butene (6f). From **3a**, MeLi, and trifluoroethanoic anhydride. Kd 35–40 °C (5 mm); 90% pure.

2-[Bis(trimethylsilyl)amino]-3-[(2-ethoxy-2-oxoethanoyl)oxy]-2-butene (6g). From **3a**, MeLi, and ethyl oxalyl chloride. Kd 40–43 °C (2 mm); over 95% pure by ^1H NMR (unstable to VPC).

2-[Bis(trimethylsilyl)amino]-3-[(ethoxycarbonyl)oxy]-2-butene (6j).[5] From **3a**, MeLi, and ethyl chloroformate. Kd 45–50 °C (2 mm); over 95% pure.

3-[Bis(trimethylsilyl)amino]-2-(ethanoyloxy)-4,4-dimethyl-2-pentene (6k). From **3a**, *t*-BuLi, and ethanoic anhydride (Ac_2O). Kd 55–60 °C (1 mm); 85% pure. Also obtained analytically pure from column chromatography, mp 140–143 °C (crystallized upon solvent removal).

2-[Bis(trimethylsilyl)amino]-3-(ethanoyloxy)-1-phenyl-2-butene (6l). From **3a**, benzyllithium,[22] and Ac_2O.

(14) Lithium bis(trimethylsilyl)amide did not behave similarly.
(15) We surmise that N-acylation may be competitive with O-acylation in some of these systems.
(16) The enamines **6** were largely destroyed (hydrolyzed to α-acyloxy ketones) upon silica gel chromatography.
(17) Later TMSOTf cyclizations employed CH_2Cl_2 as solvent; in parallel experiments, **6a** in CD_2Cl_2 was completely consumed in 2 h but some **6a** still remained after 19 h in $DCCl_3$.
(18) After 16 h in $CDCl_3$ at 25 °C, **6y** was also seen to partially cyclize to **7y**.
(19) Whitney, S. E.; Rickborn, B. *J. Org. Chem.* **1991**, *56*, 3058.
(20) Dondoni, A.; Fantin, G.; Fogagnolo, M.; Medici, A.; Pedrini, P. *J. Org. Chem.* **1987**, *52*, 3413.
(21) 2-(Chloromethyl)-5-phenyloxazole is known (Zbiral, E.; Bauer, E.; Stroh, J. *Monatsh.* **1971**, *102*, 168), as well as 2-(bromomethyl)-4,5-diphenyloxazole (Aldous, D. L.; Riebsomer, J. L.; Castle, R. N. *J. Org. Chem.* **1960**, *25*, 1151).
(22) Prepared from the metalation of toluene by *n*-BuLi–TMEDA: (a) Eberhardt, G. G.; Butte, W. A. *J. Org. Chem.* **1964**, *29*, 2928. (b) Langer, A. W., Jr. *Trans. N.Y. Acad. Sci.* **1965**, *27*, 741.

Table II. Characterization Data for Acyloxy Enamines 6 and Oxazoles 7

6	anal.	calcd	(found)	^{1}H NMR, δ; ^{13}C NMR, δ	ν (cm^{-1})	7	anal.	calcd	(found)	^{1}H NMR, δ; ^{13}C NMR, δ	ν (cm^{-1})
a	C:	52.69	(52.79)	*a*	1746 s	a		*b*		*a*	1655 m
	H:	9.95	(9.85)		1655 w			*b*		*a*	1590 s
	N:	5.12	(4.99)								
b	C:	57.09	(57.18)	*a*	1738 s	b		*b*		1.3 (s, 9 H), 2.02 (s, 3 H), 2.16	1655 m
	H:	10.54	(10.33)		1678 w					(*s*, 3 H); *a*	1565 s
	N:	4.44	(4.51)								
c	C:	60.84	(60.96)	*a*	1726 s	c		*b*		2.14 (s, 3 H), 2.30 (s, 3 H), 7.4	1640 m
	H:	8.71	(8.75)		1676 w					(m, 3 H), 7.95 (m, 2 H); *a*	1550 m
	N:	4.17	(4.26)								
d	C:	56.13	(56.30)	0.05 (s, 18 H), 1.69 (s, 3 H), 1.87	1731 s	d		*b*		1.86 (dd, J = 7 Hz, J = 1.6 Hz, 3	1660 w
	H:	9.76	(9.88)	(s, 3 H), 1.87 (m, 3 H), 5.85 (d,	1657 m					H), 2.03 (s, 3 H), 2.18 (s, 3 H),	1640 m
	N:	4.68	(4.88)	1 H), 6.97 (dq, J = 14 Hz, J =						6.16 (dq, J = 16 Hz, J = 1.6	1550 w
				7 Hz, 1 H); 2.2, 16.2, 18.0, 22.7,						Hz, 1 H), 6.56 (dq, J = 16 Hz,	1535 m
				122.9, 128.2, 137.8, 145.0, 164.5						J = 7 Hz, 1 H); 9.9, 11.1, 18.3,	
										118.1, 131.1, 133.0, 142.3	
e	C:	46.80	(46.69)	0.08 (s, 18 H), 1.70 (s, 3 H), 1.89	1742 s	e	C:	49.50	(49.58)	2.06 (s, 3 H), 2.22 (s, 3 H), 4.50	1645 m
	H:	8.51	(8.34)	(s, 3 H), 4.07 (s, 2 H); 2.1, 15.8,	1768 s		H:	5.54	(5.69)	(s, 2 H); 10.0, 11.0, 36.1,	1670 m
	N:	4.55	(4.62)	22.7, 41.0, 129.2, 137.9, 165.2						131.5, 145.0, 156.3	
f	C:	44.01	(43.91)	*a*	1788 s	f	C:	43.65	(43.86)	*a*	1640 m
	H:	7.39	(7.18)		1670 w		H:	3.66	(3.96)		1585 s
	N:	4.28	(4.44)								
g		*c*				g		*b*		*a*	1700 s
											1625 w
											1530 m
h		*c*				h	C:	66.27	(66.09)	0.90 (t, J = 7 Hz, 3 H), 1.34 (m, 2	1700 s
							H:	8.34	(8.56)	H), 1.60 (m, 2 H), 2.33 (s, 3 H),	1610 w
							N:	7.73	(7.47)	2.47 (t, J = 7 Hz, 2 H), 2.59 (s,	1515 m
										3 H); 10.4, 13.8, 22.2, 25.4, 26.2,	
										31.1, 138.3, 147.9, 156.1, 185.6	
i		*c*				i		*b*		0.87 (t, J = 7 Hz, 3 H), 1.29 (m, 2	1635 m
										H), 1.56 (m, 2 H), 2.20 (s, 3 H),	1525 s
										2.39 (t, J = 7 Hz, 2 H), 7.63 (s,	
										1 H); 9.8, 13.8, 22.2, 25.1, 31.0,	
										134.3, 143.1, 148.6	
j	C:	51.44	(51.57)	*a*	1752 s	j	C:	59.56	(59.72)	*a*; 9.7, 11.4, 14.4, 66.6, 128.9,	1600 s
	H:	9.63	(9.74)		1685 w		H:	7.85	(7.63)	137.3, 159.9	
	N:	4.61	(4.47)				N:	9.92	(9.87)		
k	C:	57.09	(57.29)	0.12 (s, 18 H), 1.17 (s, 9 H), 2.01	1736 s	k		*b*		1.25 (s, 9 H), 2.28 (s, 3 H), 2.31 (s,	1620 w
	H:	10.54	(10.66)	(s, 3 H), 2.07 (s, 3 H); 3.1, 18.4,	1635 w					3 H); 12.1, 13.7, 30.1, 31.3,	1595 m
	N:	4.44	(4.31)	21.8, 30.5, 34.9, 140.3, 168.8						140.5, 141.8, 157.5	
l	C:	61.84	(61.67)	−0.02 (s, 18 H), 2.10 (s, 3 H), 2.12	1740 s	l		*b*		2.22 (s, 3 H), 2.40 (s, 3 H), 3.78	1640 w
	H:	8.94	(9.00)	(s, 3 H), 3.34 (s, 2 H), 7.22 (m,	1668 w					(s, 2 H), 7.26 (m, 5 H); 10.0,	1585 s
	N:	4.01	(3.95)	5 H); 2.5, 16.8, 21.5, 41.4,						13.9, 32.2, 126.2, 128.47, 128.51,	
				126.4, 128.2, 129.8, 132.4,						133.3, 139.5, 143.3, 159.1	
				138.4, 138.6, 168.7							
m	C:	56.13	(56.02)	0.09 (s, 18 H), 1.89 (s, 3 H), 2.08	1740 s	m	C:	70.04	(70.00)	2.16 (s, 3 H), 2.34 (s, 3 H), 3.13	1640 w
	H:	9.76	(9.79)	(s, 3 H), 2.80 (d, J = 7 Hz, 2	1665 w		H:	8.08	(8.15)	(d, J = 6 Hz, 2 H), 5.05 (m, 2	1592 s
	N:	4.68	(4.43)	H), 5.04 (m, 2 H), 5.77 (m, 1	1634 w		N:	10.21	(10.25)	H), 5.88 (m, 1 H); 9.9, 13.8,	
				H); 2.5, 16.0, 21.3, 40.5, 116.3,						30.2, 116.0, 132.0, 135.2, 143.1,	
				130.7, 134.8, 138.1, 168.7						159.0	
n	C:	52.12	(52.40)	0.08 (s, 9 H), 0.14 (s, 18 H), 1.55	1760 s	n	C:	58.97	(59.02)	0.00 (s, 9 H), 1.73 (s, 2 H), 2.12 (s,	1635 w
	H:	10.20	(10.27)	(s, 2 H), 1.78 (s, 3 H), 2.09 (s,	1672 w		H:	9.35	(9.41)	3 H), 2.31 (s, 3 H); −1.5, 10.0,	1585 m
	N:	4.05	(4.24)	3 H); 0.0, 3.0, 16.7, 21.7, 26.9,			N:	7.64	(7.69)	13.9, 15.4, 132.4, 140.6, 158.2	
				131.0, 133.7, 168.8							
o	C:	54.68	(54.71)	0.11 (s, 18 H), 1.95 (s, 3 H), 2.14	1764 s	o	C:	68.27	(68.31)	2.26 (s, 3 H), 2.38 (s, 3 H), 5.17	1650 m
	H:	9.53	(9.59)	(s, 3 H), 5.04 (dd, J = 11 Hz,	1640 m		H:	7.37	(7.48)	(dd, J = 12 Hz, J = 2 Hz, 1	1600 m
	N:	4.91	(5.16)	J = 2 Hz, 1 H), 5.27 (dd, J =	1600 w		N:	11.37	(11.13)	H), 5.75 (dd, J = 16 Hz, J = 2	
				17 Hz, J = 2 Hz, 1 H), 6.55						Hz, 1 H), 6.43 (dd, J = 16 Hz,	
				(dd, J = 17 Hz, J = 11 Hz,						J = 12 Hz, 1 H); 10.0, 13.8,	
				1 H); 2.1, 17.0, 20.9, 115.4,						113.6, 125.1, 133.4, 144.4, 159.5	
				132.4, 133.8, 144.5, 169.0							
p	C:	53.72	(53.75)	0.12 (s, 18 H), 0.15 (s, 9 H), 1.97	1742 s	p	C:	61.49	(61.57)	0.15 (s, 9 H), 2.26 (s, 3 H), 2.33 (s,	1600 m
	H:	9.86	(10.01)	(s, 3 H), 2.11 (s, 3 H), 5.60 (d,			H:	8.77	(8.81)	3 H), 5.59 (d, J = 3 Hz, 1 H),	1585 w
	N:	3.97	(4.01)	J = 2 Hz, 1 H), 5.97 (d, J = 2			N:	7.17	(7.22)	5.78 (d, J = 3 Hz, 1 H); −1.0,	
				Hz, 1 H); 1.2, 2.4, 18.3, 22.1,						11.2, 13.8, 126.7, 137.4, 142.2,	
				131.3, 135.8, 141.5, 149.1, 168.8						143.7, 158.0	
q	C:	56.13	(56.19)	1.42 (m, 1 H), 1.98 (s, 3 H), 2.08	1758 s	q	C:	70.04	(70.13)	0.75 (m, 4 H), 1.60 (m, 1 H), 2.23	1655 w
	H:	9.76	(9.93)	(s, 3 H); 2.3, 5.6, 15.0, 16.0,	1665 w		H:	8.08	(8.26)	(s, 3 H), 2.32 (s, 3 H); 5.7, 6.3,	1595 s
	N:	4.68	(4.44)	21.4, 131.6, 139.7, 168.9			N:	10.21	(9.99)	9.9, 13.7, 135.0, 142.6, 158.7	
r	C:	60.84	(60.68)	0.09 (s, 18 H), 2.04 (s, 3 H), 2.22	1755 s	r		*b*		2.45 (s, 3 H), 2.49 (s, 3 H), 7.2–7.7	1600 s
	H:	8.71	(8.49)	(s, 3 H), 7.25–7.45 (m, 5 H);	1650 w					(m, 5 H); 11.7, 13.8, 126.5,	1590 s
	N:	4.17	(4.49)	2.2, 17.8, 21.5, 127.3, 127.5,						127.0, 128.5, 132.5, 134.4, 143.3,	
				130.0, 134.0, 139.8, 140.4						159.1	

Table II (Continued)

6	anal. calcd	anal. (found)	^{1}H NMR, δ; ^{13}C NMR, δ	ν (cm^{-1})	7	anal. calcd	anal. (found)	^{1}H NMR, δ; ^{13}C NMR, δ	ν (cm^{-1})
s	*c*				s	C: 72.82 H: 10.56 N: 7.72	(72.78) (10.56) (7.70)	0.82 (m, 3 H), 1.22 (s, 6 H), 1.5 (m, 2 H), 1.97 (s, 3 H), 2.30 (s, 3 H), 2.45 (t, *J* = 7 Hz, 2 H); 11.0, 13.8, 14.0, 22.5, 24.4, 28.2, 28.6, 31.4, 127.8, 146.7, 158.6	1640 w 1585 m
t	C: 55.76 H: 10.36 N: 4.64	(55.57) (10.63) (4.72)	0.09 (s, 18 H), 0.97 (d, *J* = 7 Hz, 6 H), 1.73 (s, 3 H), 2.08 (s, 3 H), 2.76 (m, *J* = 7 Hz, 1 H); 2.4, 20.1, 21.0, 22.5, 29.9, 127.6, 144.9, 168.9	1740 s 1660 w	t	C: 69.03 H: 9.41 N: 10.06	(68.80) (9.65) (9.79)	1.18 (d, *J* = 7 Hz, 6 H), 2.03 (s, 3 H), 2.34 (s, 3 H), 2.92 (sep, *J* = 7 Hz, 1 H); 11.1, 13.8, 21.3, 25.1, 127.9, 151.0, 158.5	1640 w 1590 m
u	*c*				u	*b*		2.07 (s, 3 H), 2.33 (s, 3 H), 3.87 (s, 2 H), 7.1–7.3 (m, 5 H); 1.11, 13.8, 30.8, 126.5, 128.3, 128.5, 131.0, 137.8, 144.7, 159.4	1645 w 1585 s
v	C: 60.84 H: 8.71 N: 4.17	(60.88) (8.56) (4.21)	0.19 (s, 18 H), 1.76 (s, 3 H), 2.07 (s, 3 H), 7.2–7.35 (m, 5 H); 2.3, 21.4, 23.8, 127.5, 127.9, 129.0, 132.1, 136.5, 140.6, 168.7	1742 m 1655 w	v	*b*		2.36 (s, 3 H), 2.46 (s, 3 H), 7.2–7.6 (m, 5 H); 13.2, 13.9, 125.1, 127.3, 128.7, 129.3, 131.6, 145.1, 159.4	1620 w 1570 s
w	*c*				w	*b*		0.89 (t, *J* = 7 Hz, 3 H), 1.33 (m, 2 H), 1.56 (m, 2 H), 2.38 (s, 3 H), 2.43 (t, *J* = 7 Hz, 2 H), 7.20 (s, 1 H); 13.8, 13.9, 22.3, 25.9, 30.4, 133.4, 141.0, 161.1	1600 m 1580 s
x	C: 66.45 H: 7.86 N: 3.52	(66.43) (7.95) (3.33)	0.21 (s, 18 H), 1.88 (s, 3 H), 7.2–7.6 (m, 8 H), 8.08 (m, 2 H); 2.3, 23.9, 127.6, 128.0, 128.3, 129.0, 129.9, 130.4, 132.5, 133.0, 136.5, 140.7, 164.6	1720 s 1650 w	x	*b*		2.52 (s, 3 H), 7.2–8.1 (m, 10 H); 13.5, 125.3, 126.2, 127.5, 127.6, 128.4, 128.7, 129.2, 130.1	1600 m 1550 m
y	*c*				y	C: 58.16 H: 3.55 N: 6.16	(58.04) (3.71) (6.16)	2.38 (s, 3 H), 7.3–7.7 (m, 5 H); 13.1, 116.7, (q, *J* = 270 Hz); 126.0, 127.5, 129.0, 132.7, 147.8, 148.2, 149.7	1585 m 1575 m
z	*c*				z	C: 69.60 H: 10.78 N: 12.49	(69.47) (10.97) (12.73)	0.95 (d, *J* = 6 Hz, 12 H), 1.13 (d, *J* = 7 Hz, 6 H), 2.33 (s, 3 H), 3.04 (sep, *J* = 7 Hz, 1 H), 3.34 (sep, *J* = 6 Hz, 2 H); 14.4, 21.1, 21.4, 23.9, 48.8, 135.6, 151.5, 156.6	1640 m 1595 m
aa	C: 51.11 H: 9.36 N: 5.42	(51.13) (9.47) (5.35)	0.09 (s, 6 H), 1.72 (s, 6 H), 1.93 (s, 6 H); 2.1, 15.6, 22.6, 129.9, 137.5, 155.9	1762 s 1738 s 1669 w	aa	C: 62.49 H: 6.29 N: 14.57	(62.36) (6.37) (14.51)	2.10 (s, 6 H), 2.27 (s, 6 H); 10.0, 11.1, 132.7, 145.1, 148.9	1620 s
bb	C: 56.71 H: 8.84 N: 4.72	(56.71) (8.65) (4.77)	0.03 (s, 36 H), 1.75 (s, 6 H), 1.97 (s, 6 H), 8.09 (s, 4 H); 2.1, 16.2, 22.8, 128.8, 129.7, 134.4, 138.0, 163.9	1733 s 1670 w	bb	C: 71.62 H: 6.01	(71.06) (6.24)	2.13 (s, 3 H), 2.29 (s, 3 H), 8.00 (m, 5 H); 10.1, 11.2, 126.0, 128.6, 132.3, 143.8, 158.6	1635 w 1610 w 1580 w

[a] See ref 5. [b] Known compound; see Experimental Section. [c] Not isolated.

4-[Bis(trimethylsilyl)amino]-5-(ethanoyloxy)-1,4-hexadiene (6m). From **3a**, allyllithium,[23] and Ac_2O. Column chromatography gave analytically pure **6m**.

2-[Bis(trimethylsilyl)amino]-3-(ethanoyloxy)-1-(trimethylsilyl)-2-butene (6n). From **3a**, [(trimethylsilyl)methyl]lithium,[24] and Ac_2O, added after 2 h at 25 °C. Kd 45–50 °C (1 mm); over 90% pure.

3-[Bis(trimethylsilyl)amino]-4-(ethanoyloxy)-1,3-pentadiene (6o). From **3a**, vinyllithium,[25] and Ac_2O. Column chromatography gave analytically pure **6o**.

3-[Bis(trimethylsilyl)amino]-4-(ethanoyloxy)-2-(trimethylsilyl)-1,3-pentadiene (6p). From **3a**, [α-trimethylsilyl)vinyl]lithium,[26] and Ac_2O. Kd 45–55 °C (2 mm); over 95% pure.

1-[Bis(trimethylsilyl)amino]-2-(ethanoyloxy)-1-cyclopropyl-1-propene (6q). From **3a**, cyclopropyllithium,[27] and Ac_2O. Column chromatography gave pure **6q** as a waxy solid.

1-[Bis(trimethylsilyl)amino]-2-(ethanoyloxy)-1-phenyl-1-propene (6r). From **3a**, phenyllithium, and Ac_2O. Column chromatography gave analytically pure **6r**.

2-[Bis(trimethylsilyl)amino]-3-(ethanoyloxy)-4-methyl-2-pentene (6t). From **4**, MeLi (initially at −78 °C), and Ac_2O. Kd 40–45 °C (1 mm); over 90% pure.

2-[Bis(trimethylsilyl)amino]-1-(ethanoyloxy)-1-phenyl-1-propene (6v). From **3d**, MeLi, and Ac_2O. Column chromatography gave analytically pure **6v**.

2-[Bis(trimethylsilyl)amino]-1-(benzoyloxy)-1-phenylpropene (6x). From **3d**, MeLi, and benzoyl chloride. Column chromatography gave analytically pure **6x**.

Bis[2-[bis(trimethylsilyl)amino]-1-methylpropenyl] Ethanedicarboxylate (6aa). A mixture of **3a** and MeLi was stirred at 25 °C for 1 h, cooled to −78 °C, and slowly treated with 0.5 equiv of oxalyl chloride. After 1 h at −30 °C, 2 h at 0 °C, and 16 h at 25 °C, workup and column chromatography gave analytically pure **6aa**, mp 57.0–58.5 °C. A low yield of impure product was obtained if the reaction temperature was allowed to rise quickly from −78 °C.

Bis[2-[bis(trimethylsilyl)amino]-1-methylpropenyl] 1,4-Benzenedicarboxylate (6bb). From **3a**, MeLi, and 1,4-benzenedicarbonyl chloride exactly as described for **6aa**, mp 94–96 °C.

General Method for the Preparation of Oxazoles 7. Trimethylsilyl Trifluoromethanesulfonate (TMSOTf) Cy-

(23) Prepared from the transmetalation of *n*-BuLi and allyltri-*n*-butyltin in ether. Method of Seyferth, D.; Weiner, M. A. *J. Org. Chem.* **1961**, *26*, 4797.

(24) Prepared from lithium dispersion (1% Na) and (chloromethyl)-trimethylsilane in ether.

(25) Prepared from vinyltri-*n*-butyltin and *n*-BuLi in TMEDA–ether. See: Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561.

(26) Prepared from (α-bromovinyl)trimethylsilane and 2 equiv of *t*-BuLi at −78 °C in ether.

(27) Prepared from bromocyclopropane and 2 equiv of *t*-BuLi in ether at −78 °C, warmed to 25 °C, and recooled to −78 °C before use.

clization. A solution of between 1.0 and 3.0 mmol of **6** and respectively 0.9–2.7 mmol of TMSOTf in $CHCl_3$ or CH_2Cl_2 (1–3 mL/mmol of **6**) was prepared under Ar, and the flask was then stoppered and sealed (Parafilm). After stirring at 25 °C for the indicated time, workup consisted of either passage through basic alumina (anhydrous workup) or partitioning between pentane–aqueous $NaHCO_3$ (aqueous workup) followed by Kugelrohr distillation or column chromatography on silica gel (hexane to 5% ether–hexane).

Cyclization by Flash Vacuum Pyrolysis (FVP). Acyloxy enamines **6** were volatilized (with air-bath heating if necessary) into a 14 in. × 0.25 in. quartz Vigreux tube held at 625 °C under 1 mmHg. The pyrolysate was condensed at −78 °C. Kugelrohr distillation (Kd) followed, but the attendant hexamethyldisiloxane (HMDS) could rarely be efficiently separated from the low-boiling examples of **7** with this technique, and the product purities listed below mainly reflect its presence. See, however, the procedure for **7a**.

2,4,5-Trimethyloxazole (7a).[28] See text. Kd 65–70 °C (80 mm); 40% pure. Chromatography on silica gel (2 cm × 15 cm) of the **7a**–HMDS mixture obtained from FVP of 2.1 g of **6a** removed all but 4% of the HMDS upon hexane elution. Subsequent ether elution followed by careful distillation of the eluate gave a 79% yield of **7a**. Slight decomposition of the oxazole during chromatography was evidenced by a yellow discoloration at the column head and traces of new materials in the eluate showing ^1H NMR absorptions at δ 0.13 (s) and 7.33 (s).

4,5-Dimethyl-2-(1,1-dimethylethyl)oxazole (7b).[5,29]

4,5-Dimethyl-2-phenyloxazole (7c).[30] Two-day reaction time. Kd 40–45 °C (50 mm), 80% pure.

4,5-Dimethyl-2-(1(*E*)-propenyl)oxazole (7b).[31] FVP at 575 °C. Kd 40–50 °C (50 mm), 80% pure.

2-(Chloromethyl)-4,5-dimethyloxazole (7e). FVP at 575 °C. Kd 40–45 °C (50 mm), 76% pure.

4,5-Dimethyl-2-(trifluoromethyl)oxazole (7f). FVP at 575 °C. ^1H NMR shows only **7f** and hexamethyldisiloxane; purified by preparative VPC only.

2-Carbethoxy-4,5-dimethyloxazole (7g).[5] Kd 45–50 °C (50 mm); 70% pure.

4-Butyl-2-ethanoyl-5-methyloxazole (7h). A solution of 0.88 g (4.0 mmol) **3a** in 20 mL of ether was treated with *n*-BuLi (4.4 mmol) and stirred at 25 °C for 2 h. The mixture was cooled to −78 °C and dropwise addition of 0.47 g (4.4 mmol) of pyruvyl chloride[32] in 10 mL of ether was carried out. After warming to 25 °C, the crude **6h** obtained from an anhydrous workup was refluxed in $CHCl_3$ overnight. Kd 70–75 °C (2 mm); 82% pure.

4-Butyl-5-methyloxazole (7i)[33] was prepared as for **7h**, except that 1 equiv of trimethylacetic formic anhydride[34] was used as the acylating agent. The crude **6h** was cyclized over 5 days, followed by an aqueous workup. Kd 30–40 °C (20 mm); 65% pure.

2-Ethoxy-4,5-dimethyloxazole (7j). A sealed tube containing **6j** was heated at 140 °C for 2 d. Kd 35–40 °C (50 mm); 70% pure. Neither FVP nor TMSOTf treatment of **6j** afforded **7j**, although **7j** appeared to be present (NMR analysis) under the latter conditions before workup.

4-(1,1-Dimethylethyl)-2,5-dimethyloxazole (7k).[35] Kd 35–40 °C (50 mm); 70% pure.

2,5-Dimethyl-4-(phenylmethyl)oxazole (7l).[36] Kd 55–65 °C (1 mm); 90% pure.

2,5-Dimethyl-4-(3-propenyl)oxazole (7m). Two-day reaction time. Kd 55–65 °C (100 mm); 70% pure.

2,5-Dimethyl-4-[(trimethylsilyl)methyl]oxazole (7n). The crude enamine from **3a**, [(trimethylsilyl)methyl]lithium, and Ac_2O was subjected to FVP. Kd 45–50 °C (10 mm), 55% pure.

4-Ethenyl-2,5-dimethyloxazole (7o). Kd 40–45 °C (50 mm); 65% pure.

2,5-Dimethyl-4-[1-(trimethylsilyl)ethenyl]oxazole (7p). Three-day reaction time. Kd 45–50 °C (50 mm); 80% pure.

4-Cyclopropyl-2,5-dimethyloxazole (7q). Five-day reaction time using crude **6g**, aqueous workup. Kd 55–65 °C (100 mm); 70% pure.

2,5-Dimethyl-4-phenyloxazole (7r).[35] Kd 50–60 °C (1 mm); 90% pure.

5-Hexyl-2,4-dimethyloxazole (7s). The crude enamine from **3b**, MeLi, and Ac_2O was used; 3-day reaction time followed by aqueous workup. Kd 50–55 °C (8 mm); 85% pure.

2,4-Dimethyl-5-(1-methylethyl)oxazole (7t). Five-day reaction time followed by aqueous workup. Kd 60–75 °C (50 mm); 80% pure.

2,4-Dimethyl-5-(phenylmethyl)oxazole (7u).[36] The crude enamine from **3c**, MeLi, and Ac_2O was used; 2-day reaction time followed by aqueous workup. Kd 75–80 °C (6 mm), 80% pure.

2,4-Dimethyl-5-phenyloxazole (7v).[37] The crude enamine from **3d**, MeLi, and Ac_2O was used, 4-day reaction time. Kd 55–60 °C (1 mm); 90% pure.

4-Butyl-2-methyloxazole (7w).[38] The crude enamine from **3e**, *n*-BuLi, and Ac_2O was used; 5-day reaction time followed by aqueous workup. Kd 45–50 °C (20 mm); 75% pure.

4-Methyl-2,5-diphenyloxazole (7x).[39] The crude enamine from **3d**, PhLi, and benzoyl chloride was used; 5-day reaction time. Column chromatography gave pure **7x**.

4-Methyl-5-phenyl-2-(trifluoromethyl)oxazole (7y). The crude enamine from **3d**, MeLi, and trifluoroethanoic was used; 2-day reaction time. Kd 45–50 °C (1 mm); 84% pure.

4-[Bis(1-methylethyl)amino]-2-methyl-5-(1-methylethyl)oxazole (7z). A mixture of 1.6 g (14 mmol) TMEDA and LDA (prepared from 28 mmol of diisopropylamine and 28 mmol of *n*-BuLi) in 25 mL of THF at −78 °C was treated dropwise with a solution of 2.2 g (15 mmol) of **2** (R^5 = *i*-Pr) and 1.5 g (14 mmol) of trimethylchlorosilane in 25 mL of THF at −78 °C. After 2 h at −78 °C, the mixture was stirred at 25 °C for 2 days and Ac_2O (14 mmol) was added. An anhydrous workup (Celite filtration) was followed by stirring of the crude enamine with 0.5 mL of TMSOTf in 20 mL of CH_2Cl_2 at 25 °C for 7 days. Aqueous workup followed by column chromatography (10% ether–hexane) gave 1.62 g of **7z**; 85% pure.

2-[2-(4,5-Dimethyloxazoyl)]-4,5-dimethyloxazole (7aa). Fourteen-day reaction time using **6aa**. Aqueous workup and column chromatography gave **7aa**, mp 157–159 °C [from $CHCl_3$–cyclohexane and sublimation (100 °C/0.3 mm)].

1,4-Bis[2-(4,5-dimethyloxazolyl)]benzene (7bb). As for **6bb**; mp 248–250 °C dec (from CH_2Cl_2 by slow evaporation).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(28) Brown, D. J.; Ghosh, P. B. *J. Chem. Soc. B* **1969**, 270.
(29) Bowie, J. H.; Donaghue, P. F.; Rodda, H. J. *J. Chem. Soc. B* **1969**, 1122.
(30) Friedman, B. S.; Sparks, M.; Adams, R. *J. Am. Chem. Soc.* **1937**, *59*, 2262.
(31) Iwakura, Y.; Toda, F.; Suzuki, H.; Kusakawa, N.; Yagi, K. *J. Polym. Sci. A* **1972**, *10*, 1133.
(32) Synthesis of α-keto acid chloride: Ottenheijm, H. C. J.; DeMan, J. H. M. *Synthesis* **1975**, 163.
(33) Ho, C. T.; Tuorto, R. M. *J. Agric. Food Chem.* **1981**, *29*, 1306.
(34) Vlietstra, E. J.; Zwikker, J. W.; Nolte, R. J. M.; Drenth, W. *Recl. Trav. Chim.* **1982**, *101*, 460.
(35) Wiley, R. H. *J. Org. Chem.* **1947**, *12*, 43.
(36) Brodereck, H.; Gompper, R.; Reich, F. *Chem. Ber.* **1960**, *93*, 1389.
(37) Brodereck, H.; Gompper, R.; Reich, F. *Chem. Ber.* **1960**, *93*, 723.
(38) Ho, C. T.; Jin, Q. Z. *J. Agric. Food Chem.* **1983**, *31*, 180.
(39) Cleland, G. H.; Niemann, C. *J. Am. Chem. Soc.* **1949**, *71*, 841.