composed to starting olefin and some undetermined tin compound: IR (CCl_4) 3060 (m), 2960 (s), 2920 (s), 1600 (w), 1485 (m), 1470 (m), 1450 (m), 1380 (m), 1220 (w), 1070 (m), 860 (m), and 690 (m) cm^{-1}; ^1H NMR (CCl_4) δ 0.2-1.7 (m, 31.8 H), 2.45 (q, J = 7 Hz, 1.8 H), 4.28 (t, J = 7 Hz, 0.9 H), 6.5-7.5 (m, 13 H).

Anal. Calcd for $C_{35}H_{48}Sn$: C, 71.57; H, 9.23; Sn, 20.20. Found: C, 71.75; H, 8.16; Sn, 20.02.

Cleavage of the Tri-*n*-butyltin Hydride Adduct. To a solution of 100 mg (0.170 mmol) of the tri-*n*-butyltin hydride adduct and 5 mL of carbon tetrachloride was added 0.5 mL of trifluoroacetic acid, and the solution was allowed to stand at room temperature for 4 h. The solvent was removed on the rotary evaporator, and the product chromatographed on a 20 × 20 TLC plate with pentane/benzene (8/2) to give two bands. Band I (highest R_f) was shown by IR and NMR spectra to be a 7:93 ratio of *cis*- and *trans*-9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene. Band II was the only other band present and the NMR and IR spectra indicated it to be tri-*n*-butylstannyl trifluoroacetate. No starting material was present on the thin-layer plate and no other products were observed.

Reduction of Tri-*n*-butyltin Hydride Adduct with Tri-*n*-butyltin Hydride. A solution of 80 mg (0.103 mmol) of tri-*n*-butyltin hydride adduct and 300 mg (1.03 mmol) of tri-*n*-butyltin hydride was placed in a tube under an atmosphere of nitrogen and heated for 23 h at 164 °C. The crude reaction product was chromatographed on a 20 × 40 TLC plate with pentane/benzene (92/8) as the eluent. Band III contained 9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene in a cis-trans ratio of 39:61. No starting material was observed in any of the other bands.

The Addition and Reduction Reaction of 9-Methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene with Tri-*n*-butyltin Hydride. A tube containing a solution of 300 mg (1.03 mmol) of tri-*n*-butyltin hydride and 200 mg (0.675 mmol) of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene was placed under an atmosphere of nitrogen, sealed, and heated at 164 °C for 5 h. Some of the crude product (250 mg) was chromatographed on a 20 × 20 TLC plate with pentane/benzene (92/8). Band I (highest R_f) was tin hydride, band II was the tri-*n*-butyltin hydride adduct, and band III was a mixture of starting olefin and a 41:59 ratio of *cis*- and *trans*-9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene. The *tri-n*-butyltin hydride adduct obtained in band II was dissolved in carbon tetrachloride and hydrolyzed with trifluoroacetic acid. After hydrolysis, the product was chromatographed with thin-layer techniques previously described. The hydrocarbon fraction was isolated and shown to be 93% *trans*-9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene. Band II contained tri-*n*-butylstannyl fluoroacetate.

Procedure for Studying Nuclear Overhauser Effect. The spectra was recorded on a Bruker HFX-10 spectrometer in the frequency sweep mode. The sample was dissolved in carbon tetrachloride and contained chloral as the internal field frequency lock. It was degassed with the freeze-thaw method and sealed. The power requirement of the irradiating frequency was determined by increasing the power until the protons coupled to the irradiated protons were completely decoupled. The peak was then integrated four times with the same power level but with the irradiating frequency offset 30 Hz from the original irradiation.

Registry No. 2, 17407-18-0; 3, 92844-32-1; *trans*-4 (X = H; Y = PhS), 92844-39-8; *cis*-4 (X = H; Y = PhS), 92844-40-1; 4 (X = H; Y = Bu_3Sn), 92844-41-2; *trans*-8, 92844-34-3; *cis*-8, 92844-35-4; *trans*-9, 92844-36-5; *cis*-9, 92844-38-7; PhSH, 108-98-5; EtBr, 74-96-4; Bu_3SnH, 688-73-3; 9-phenyl-10-(2-phenyl-2-methylpropyl)anthracene, 92844-33-2; 9-phenylanthracene, 602-55-1; 10-ethyl-10-phenylanthrone, 17407-19-1; 9-ethylidene-10-ethyl-10-phenyl-9,10-dihydroanthracene, 92844-37-6.

Nucleophilic Ring Opening of 2-Oxazolines with Amines: A Convenient Synthesis for Unsymmetrically Substituted Ethylenediamines

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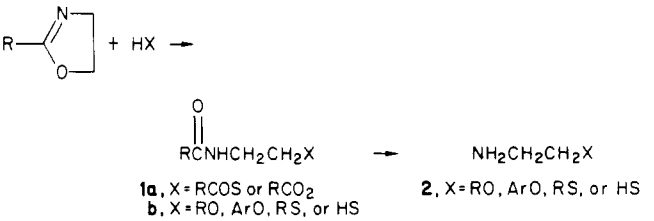
Received February 29, 1984

The reaction of 2-alkyl-2-oxazolines with alkyl- and arylamines was investigated. The acid-catalyzed nucleophilic ring opening of the 2-oxazolines yields *N*-(2-aminoethyl)carboxamides in good to excellent yields with secondary amines and hindered primary amines. The *N*-(2-aminoethyl)carboxamides were hydrolyzed under acidic or basic conditions to selectively yield unsymmetrically substituted ethylenediamines.

2-Oxazolines are versatile chemical intermediates.[1] The ring opening of oxazolines by nucleophiles was first reported in 1950 by Fry[2] and subsequently by several others.[3-6] The nucleophilic ring opening at the 5-position yields β-substituted ethylcarboxamides 1. Hydrolysis of the carboxamides **1b** yields 2-substituted ethylamines **2**. Oxazolines can, therefore, be viewed as an aminoethylation reagent or the synthetic equivalent of aziridine.



In our continuing study of oxazoline chemistry we have investigated the ring opening of oxazolines by primary and

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(2) Fry, E. M. *J. Org. Chem.* **1950**, *15*, 802.

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Scheme I

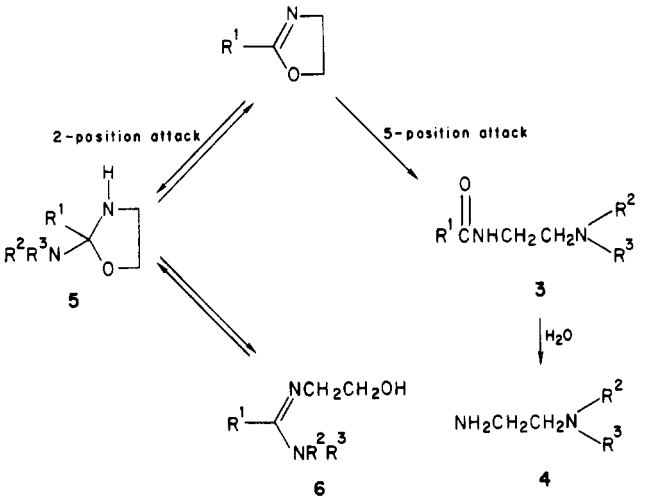


Table I. Catalysts Examined for the Reaction of 2-Ethyl-2-oxazoline and Diethylamine[a]

cat.	conversn, % amine	conversn, % 7	yield[b] of 8, %
	15	15	8
H_2Wo_3	69	76	63
$Fe_2(SO_4)_3$	95	100	79
$CdCl_2$	95	100	80
$Zn(OAc)_2$	93	100	84
$CoCl_2$	93	100	86
$CH_3C_6H_4SO_3H$	98	100	86
$BF_3{\cdot}Et_2O$	98	100	89

[a] Reaction conditions: 225 °C and 19 h. [b] Analytical yields determined by internal standard GLC.

secondary amines.[7] Our objective was to develop a convenient synthesis for unsymmetrically substituted ethylenediamines.

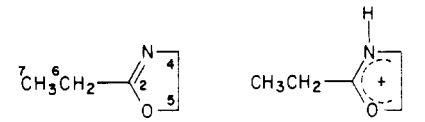
The reported reactions of oxazolines with amines show aliphatic amines, ammonia,[8] and 1,2- and 1,3-alkylenediamines[9] react to yield products derived from attack at the 2-position of the oxazoline. Aromatic amines are reported to yield products of attack at both the 2- and 5-positions.

The premise for our work on the reaction of oxazolines with amines was based on the belief that the selectivity for products formed by reaction at the 5-position vs. the 2-position could be controlled (Scheme I). Reaction at the 2-position would yield oxazolidine (**5**) and *N*-(2-hydroxyethyl)amidine (**6**), analogous to the reaction of acyclic imidates with amines.[11] Lambert and Kristofferson[12] have demonstrated that oxazolines can be prepared from *N*-(2-hydroxyethyl)butyramidine, which suggests addition at the 2-position is a reversible reaction.

Results and Discussion

Reactions of Oxazolines with Secondary Aliphatic Amines. Reactions of equimolar amounts of a 2-oxazoline and secondary amine at 220–225 °C for 19 h yields *N*-(2-aminoethyl)carboxamides in low yield. The conversions of diethylamine and 2-ethyl-2-oxazoline (**7**) were only 15%,

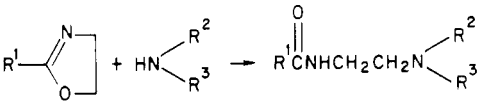
Table II. ^{13}C NMR Chemical Shifts (ppm)[a]



carbon	δ	δ	Δδ
2	168.4	182.3	−13.9
4	55.0	45.7	+9.3
5	67.4	73.8	−6.4
6	21.5	21.2	+0.3
7	10.5	8.0	+2.5

[a] Relative to Me_4Si.

Table III. Reaction of 2-Substituted 2-Oxazolines with Secondary Amines[a]



R^1	R^2	R^3	yield[b] of amide, %
Et	Et	Et	84
Et	*n*-Bu	*n*-Bu	85
Et	$-(CH_2)_2O(CH_2)_2-$		82
Et	$-(CH_2)_6-$		93
Ph	Et	Et	70
$C_{11}H_{23}$	Et	Et	89

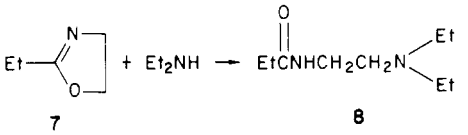
[a] Reaction conditions: 205 °C, 24 h, and 1 mol % zinc acetate. [b] Analytical yields detemined by internal standard GLC.

Table IV. Effect of Temperature on the Reaction of 2-Ethyl-2-oxazoline and Diethylamine

temp, °C	yield[a] of 8, %	$t_{1/2}$, min
180	92	264
205	86	90
225	81	42

[a] Analytical yields determined by internal standard GLC.

and the yield of *N*-(2-(diethylamino)ethyl)propionamide (**8**) based on starting materials was 8%. The ring opening



7 **8**

was catalyzed by Brønsted and Lewis acids. Formation of the ambident oxazolinium cation[13] by protonation or coordination of the oxazoline with a Lewis acid increases the electrophilic character of this heterocycle. Spectroscopic examination of 2-ethyl-2-oxazolinium trifluoroacetate and **7** by carbon-13 NMR shows that the 2-position and 5-position of the oxazolinium salt are deshielded and more susceptible to nucleophilic addition (Table II).[14] The reaction of **7** with diethylamine yields **8** in 83% yield using 1 mol % zinc acetate as a catalyst. The reaction was carried out at 185–190 °C and the conversions of **7** and diethylamine were 93% and 83%, respectively. Table I lists the catalysts examined. Changes in the amine or 2-position of the oxazoline have no significant effect on the

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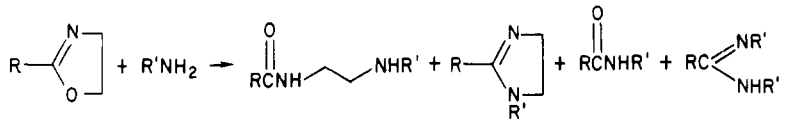
(10) Kormendy, K.; Sohar, P.; Volford, J. *Ann. Univ. Sci. Budap. Rolando Eotvos Nominatae, Sect. Chim.* **1962**, *4*, 61.
(11) Hand, E. S.; Jencks, W. P. *J. Am. Chem. Soc.* **1968**, *90*, 4413.
(12) Lambert, R. L.; Kristofferson, C. E. *J. Org. Chem.* **1965**, *30*, 3938.
(13) The relative concentrations of oxazolinium cation and amine salt are dependent upon the relative base strengths of the oxazoline and amine to be reacted. The pK_a for 2-methyl-2-oxazoline is 5.52; Weinberger, M. A.; Greenhalgh, R. *Can. J. Chem.* **1963**, *41*, 1038. Phenyl-2-oxazoline and 2-ethyl-2-oxazoline, pK_a = 4.70 and 5.75; Elguero, J.; Gonzalez, E.; Imbach, L.; Jacquier, R. *Bull. Soc. Chim. Fr.* **1969**, *11*, 4076.
(14) Assignments for carbons 4 and 5 were made on the basis of spectral data obtained on 2-ethyl-5-methyloxazoline.

Table V. Reaction of 2-Oxazolines with Primary Amines[a]



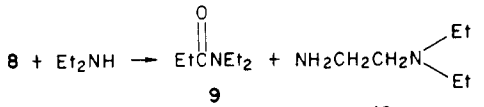
11 12 13 15

	R	R'	product distribution,[b] % 11	12	13	15
a	Et	$CH_3(CH_2)_3$	10	37	17	35
b	Et	$(CH_3)_2CH$	76	24		
c	Et	$(CH_3)_3C$	99	<1		
d	$(CH_3)_3C$	$CH_3(CH_2)_3$	100			

[a] Equimolar mixture heated with 1 mol % $Zn(OAc)_2$ at 180 °C for 3 h. [b] As determined by GC–mass spectrometry.

reaction (Table III). Good yields were observed in all cases, a marked contrast to the results obtained by the ring opening of aziridines with amines.[15]

The effect of temperature on the reaction of diethylamine and 7 is shown in Table IV. The selectivity of the reaction (moles of desired product/mole of 7 reacted) increased as the reaction progressed at 180 °C. The increase in selectivity is presumably due to the initial formation of intermediates such as 5 and 6 which ultimately decomposes back to starting materials and then converted to 8. At 225 °C the selectivity decreases as the reaction proceeds and *N,N*-diethylpropionamide (9) and 2-(diethylamino)-ethylamine (10) were observed presumably formed by the transamidation[16] of 8 with unreacted diethylamine. Pure 8 is recovered unchanged after heating at 200 °C for 12 h with 1 mol % zinc acetate; no 7 or diethylamines was observed.



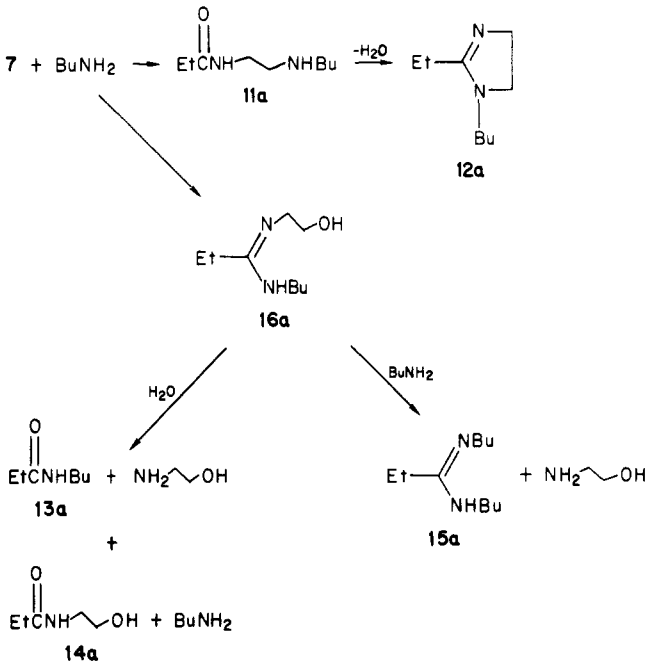
9 10

Reaction of Oxazolines with Primary Aliphatic Amines. *n*-Butylamine reacts with 7 to yield a complex mixture (Scheme II). The desired product **11a** is obtained in 3% yield and 1-butyl-2-ethyl-2-imidazoline (**12a**) in 30% yield. The other products identified are *N*-butylpropionamide (**13a**), *N*-(2-hydroxyethyl)propionamide (**14a**), *N,N'*-dibutylpropionamidine (**15a**), and ethanolamine. The formation of amidine **16a**, addition at the 2-position, is favored when *n*-butylamine and 7 are reacted. The formation of **16a** was observed at temperatures as low as 40 °C. *tert*-Butylamine, however, reacts with 7 to yield *N*-(2-*tert*-butylamino)ethyl)propionamide in 53% yield.

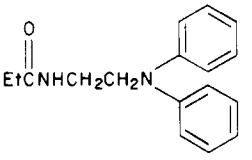
The influence of steric effects in both amine and oxazoline is shown in Table V. As the bulkiness of the amine increases, the cyclodehydration of 11 to 12 decreases dramatically. The secondary reaction products 13 and 15 are observed only in the reaction of *n*-butylamine with 7. Blocking the 2-position of the oxazoline ring with a *tert*-butyl group forces even unhindered amines such as *n*-butylamine to react at the 5-position to yield **11d** as the only observed product.

Reaction of Oxazolines with Arylamines. The reaction of *N*-ethylaniline with 7 under the conditions used to prepare 8 yields poly(*N*-propionylethylene imine)[17] as

Scheme II



the main product. The desired product *N*-ethyl-*N*-(2-propionamidoethyl)aniline (**17**) is formed in only 13% yield. High yields of 17 are, however, achieved when the concentration of oxazoline relative to arylamine is low. The slow addition of 7 to *N*-ethylaniline at 180 °C yielded 17 in 87% yield. *N*-ethyl-*m*-toluidine reacts with 7 in a similar fashion, at 160 °C using hydrochloric acid as the catalyst, yielding *N*-ethyl-*N*-(2-propionamidoethyl)-*m*-toluidine (**18**) in 98% yield. This procedure is also applicable to sterically hindered weak bases such as diphenylamine. The reaction of 7 with diphenylamine yields *N*-phenyl-*N*-(2-propionamidoethyl)aniline (**19**). Primary



19

arylamines react with 7 in a similar manner. The initial product is a secondary amine which can react with a second mole of oxazoline to yield bis(amidoethylated) products. Equimolar amounts of aniline and 7 give a 10:87:3 mixture of aniline, **20**, and **21**.

Hydrolysis of *N*-(2-Aminoethyl)carboxamides. Carboxamides 3 were hydrolyzed by classical techniques to yield substituted ethylenediamines. Hydrolysis under

(15) Dermer, O. C.; Ham, G. E. "Ethylenimine and Other Aziridines"; Academic Press: New York, 1969; pp 237–239.
(16) (a) Sowa, F. J.; Nieuwland, J. A. *J. Am. Chem. Soc.* **1937**, *59*, 1202. (b) Galat, A.; Elion, G. *J. Am. Chem. Soc.* **1943**, *65*, 1566.
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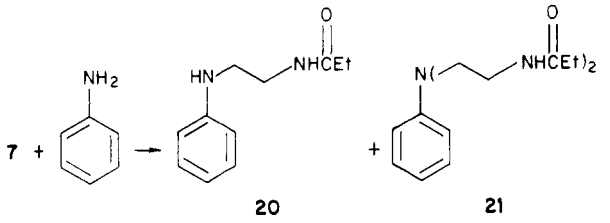
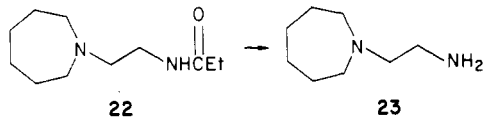


basic conditions is preferred since the free amine formed can readily be isolated by extraction and purified by distillation although acid hydrolysis, which yields the amine salt, is faster than base hydrolysis. The conversion of 8 after refluxing in aqueous sodium hydroxide for 40 h was 99%. The reaction time can be decreased by conducting the hydrolysis at higher temperatures under pressure. Hydrolysis of *N*-(2-(hexamethyleneimino)ethyl)propionamide (**22**) to 2-(hexamethyleneimino)ethylamine (**23**) was complete after 16 h at 170 °C. The hydrolysis of *N*-(2-aminoethyl)carboxamides with poor water solubility is significantly accelerated by the use of a cosolvent such as ethanol.



Summary

The reaction of oxazolines with amines provides a convenient alternative to the reported synthesis of substituted ethylenediamines based on aziridine,[15,19b] phthalimide alkylations,[18,19a] nitrile reduction,[19] or Hofmann rearrangement of 2-aminopropionamides.[20] The acid-catalyzed ring opening of 2-oxazolines by amines yields *N*-(2-aminoethyl)carboxamides by the irreversible addition at the 5-position. Addition of amine at the 2-position of the 2-oxazoline is a competitive reaction but is reversible. Hydrolysis of the carboxamides under acidic or basic conditions yields the corresponding diamines. The reaction proceeds in good to excellent yields with secondary alkyl- and arylamines and hindered primary amines.

Experimental Section

Proton NMR spectra were recorded on a Varian T-60 spectrophotometer with tetramethylsilane as an internal standard. Carbon NMR spectra were recorded on a 15-MHz JEOL JNM-FX60 spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer 598 spectrophotometer. Melting points were determined on a Thomas Hoover capillary apparatus and are uncorrected. Elemental analysis was performed by the Analytical Laboratories of the Dow Chemical Co. Gas–liquid chromatography was carried out on a Hewlett Packard 5730A chromatograph using a 10-ft glass column packed with 10% UCW-98 on 80/100 GCQ. An Excalibar Spherisorb CN, 5 μm (25 cm × 4.6 mm) column was used for high-pressure liquid chromatography with a LDC UV-III detector (214 nm). Mass spectral data were obtained on a Finnigan 4021 gas chromatography mass spectrometer.

***N*-(2-(Diethylamino)ethyl)propionamide (8).** A 45-mL Parr reactor was charged with 15.7 g (0.16 mol) of 2-ethyl-2-oxazoline,[21] 11.5 g (0.16 mol) of diethylamine, and 0.36 g of $Zn(OAc)_2 \cdot 2.5H_2O$. The reactor was purged with N_2, sealed, and heated to 185–190 °C for 17 h. The reactor was then cooled to room temperature. The propionamide **8**, 21.8 g (80% yield), was recovered by distillation at reduced pressure; bp 93–94 °C (0.5 mmHg) [lit.[22] bp 77–78 °C (0.2 mmHg)]. Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.0 and 1.08 (9 H, overlapping t), 2.21 (2 H, q), 2.52 (6 H, m), 3.25 (2 H, q), 6.8 (1 H, br s); IR (neat) 3290, 2960, 1645, 1540 cm^{-1}.

2-(Diethylamino)ethylamine (10). A mixture of 124 g of **8** (assay 90%, 0.65 mol), 80 g of 50% NaOH, and 250 mL of water were refluxed under N_2. After 40 h the mixture was cooled to room temperature and extracted with chloroform (100 mL × 4). The extracts were combined, dried (Na_2SO_4), and evaporated. The crude oil was distilled at reduced pressure; 57 g (76% yield) of **10**, bp 55–57 °C (40 mmHg) [lit.[23] bp 144–145 °C], was recovered. Spectral data: ^{1}H NMR ($CDCl_3$) δ 0.98 (6 H, t), 1.25 (2 H, s), 2.55 (8 H, m); IR (neat) 3300, 2960, 2800, 1590, 1450, 1380, 1200, 1060 cm^{-1}.

***N*-Ethyl-*N*-(2-propionamidoethyl)-*m*-toluidine (18).** A mixture of 100.3 g (0.74 mol) of *N*-ethyl-*m*-toluidine and 6.2 g (36 mmol) of *N*-ethyl-*m*-toluidine hydrochloride was heated to 160 °C under N_2. Ethyloxazoline (77.6 g, 0.78 mol) was then slowly added. The addition took 4 h, and the mixture was heated for 1 h at 160 °C. The mixture solidified on cooling. Analysis by liquid chromatography (93/7 hexane–2-propanol) showed the crude product, 183.6 g, was 98 wt % **18** (98% yield). A sample of the crude product was recrystallized from cyclohexane; mp 69–70 °C. Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.1 (6 H, m), 2.15 (q) and 2.48 (s) (combined 5 H), 3.33 (6 H, m), 5.8 (1 H, br s), 6.4 (3 H, m), 6.9 (1 H, m). Anal. Calcd for $C_{14}H_{22}N_2O$: C, 71.79; H, 9.40; N, 11.97. Found: C, 71.5; H, 9.42; N, 11.83.

***N*-(2-Aminoethyl)-*N*-ethyl-*m*-toluidine (28).** The crude **18** (46.1 g), 100 mL of 10% NaOH, and 100 mL of ethanol were charged into a 1-L nickel Parr reactor, purged with N_2, and heated to 150 °C. At reaction temperature the reactor pressure was 100 psig. After being heated for 9 h, the reactor was cooled and the reaction mixture recovered. Ethanol was stripped at reduced pressure, and the product was extracted from the hydrolysis mixture with chloroform (100 mL × 2). The solvent was evaporated to yield 36.6 g of a brown oil. The crude product, 34.5 g, was distilled at reduced pressure through a 6 in. Vigreaux column. Pure **28** (28.9 g (82% yield); bp 70–73 °C (0.1 mmHg) [lit.[24] bp 120 °C (3 mmHg)]) was isolated. Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.1 (5 H, t) (3 H after D_2O wash), 2.27 (3 H, s), 2.83 (2 H, t), 3.27 (4 H, m), 6.47 (3 H, m), 7.0 (1 H, m). Anal. Calcd for $C_{11}H_{18}N_2$: C, 74.16; H, 10.11; N, 15.73. Found: C, 74.0; H, 10.35; N, 15.82.

***N*-(2-(Dibutylamino)ethyl)propionamide (24).** *n*-Dibutylamine (13.1 g, 100 mmol), 10.1 g (100 mmol) of **7**, and 300 mg of zinc acetate were allowed to react at 180 °C for 24 h in a pressure reactor. The product, 14.6 g (64% yield), was isolated by distillation; bp 124–126 °C (0.4 mmHg). Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.8 (17 H, m), 2.45 (8 H, m), 3.25 (2 H, q), 6.23 (1 H, br s); IR (neat) 3280, 2940, 1645, 1545, 1465 cm^{-1}.

2-(Dibutylamino)ethylamine (29). Distilled **24** (14.6 g, 64 mmol), 20 mL of concentrated HCl, and 100 mL of water were refluxed overnight. The mixture was cooled, concentrated, basified (NaOH), and extracted with chloroform. The extract was dried over $MgSO_4$ and then distilled at reduced pressure. Pure **29**, 8 g (73% yield), was recovered; bp 105–106 °C (9.5 mmHg) [lit.[25] bp 99–102 °C (17 mmHg)]. Spectral data: ^{1}H NMR ($CDCl_3$) δ 0.9 (6 H, m), 1.33 (10 H, m) (8 H after D_2O wash), 2.53 (8 H, m). Anal. Calcd for $C_{10}H_{24}N_2$: C, 69.77; H, 13.95; N, 16.28. Found: C, 69.9; H, 14.21; N, 16.28.

***N*-(2-Morpholinylethyl)propionamide (25).** Morpholine (11.8 g, 140 mmol), 13.3 g (130 mmol) of **7**, and 270 mg of zinc acetate were heated for 24 h at 180 °C. The crystalline reaction mixture was recrystallized from diethyl ether. Isolated **25**, 17 g (70% yield), had a melting point of 84–84.5 °C [lit.[26] mp 85 °C].

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Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.13 (3 H, s), 2.22 (2 H, q), 2.43 (6 H, m), 3.3 (2 H, q), 3.65 (4 H, m), 6.0 (1 H, br s); IR (neat) 3390, 2930, 1640, 1545, 1455, 1110 cm^{-1}.

***N*-(2-(Diethylamino)ethyl)benzamide (26).** 2-Phenyl-2-oxazoline (20 g, 0.14 mol), 10 g (0.14 mol) of diethylamine, and 400 mg of zinc acetate were reacted for 24 h at 180 °C. The product **26**, 15.8 g (51% yield), was isolated by distillation, bp 135–137 °C (0.5 mmHg) [lit.[27] bp 142–146 °C (1 mmHg)]. Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.02 (6 H, t), 2.7 (6 H, q), 3.43 (2 H, q), 6.93 (1 H, br s), 7.3 (3 H, m), 7.63 (2 H, m); IR (neat) 3320, 2970, 1640, 1600, 1580, 1540, 1490, 1300 cm^{-1}.

***N*-(2-(Diethylamino)ethyl)dodecylamide (27).** Diethylamine (5.6 g, 77 mmol), 15.1 g (67 mmol) of 2-undecyl-2-oxazoline, and 250 mg of zinc acetate were allowed to react for 36 h at 180 °C. The product, 17.6 g (88% yield), crystallized from acetonitrile; mp 31.5–32 °C. Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.0 (t) and 1.27 (m) (combined 27 H), 2.3 (8 H, m), 3.23 (2 H, q), 6.03 (1 H, br s); IR (neat) 3290, 2910, 2840, 1640, 1545, 1465 cm^{-1}. Anal. Calcd for $C_{18}H_{38}N_2O$: C, 72.48; H, 12.75; N, 9.40. Found: C, 72.67; H, 12.73; N, 9.25.

***N*-(2-(Hexamethyleneimino)ethyl)propionamide (22).** Hexamethyleneimine (10 g, 102 mmol), 10 g (101 mmol) of **7**, and 200 mg of zinc acetate were heated to 190 °C for 16 h. The product, 17.7 g (89% yield), was isolated by distillation; bp 113–114 °C (0.08 mmHg). Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.13 (3 H, t), 1.57 (8 H, s), 2.27 (2 H, q), 2.57 (6 H, m), 3.25 (2 H, q), 6.47 (1 H, br s); IR (neat) 3380, 2920, 1645, 1550 cm^{-1}.

2-(Hexamethyleneimino)ethylamine (23). Crude **22** (5 g, 24 mmol) and 11 g of 10% NaOH were heated under N_2 in a 45-mL Parr reactor to 170 °C. After 16 h the reaction mixture was cooled and extracted with methylene chloride (20 mL × 3). The extracts were combined, dried (Na_2SO_4), and evaporated. The oil recovered, 3.3 g, was 91 wt % **23** by GLC analysis (89% yield). Distillation yielded pure 23, bp 43–44 °C (0.35 mmHg) [lit.[19b] bp 66–67 °C (2 mmHg)]. Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.35 (2 H, s), 1.58 (8 H, s), 2.58 (8 H, m).

***N*-Ethyl-*N*-(2-propionamidoethyl)aniline (17).** *N*-Ethylaniline (11.5 g, 95 mmol) and 0.87 g (5 mmol) of *N*-ethylaniline hydrochloride were heated to 180 °C under N_2. Ethyloxazoline (9.9 g, 0.1 mol) was then added over a period of 1 h and heated for an additional hour. The crude product solidified on cooling. Eleven grams of the crude product were taken up in chloroform and washed with aqueous NaOH. Chloroform was evaporated, and the product was recrystallized from diethyl ether to yield 9.6 g of **17**, mp 79–80 °C. Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.08 (6 H, t), 2.13 (2 H, q), 3.33 (6 H, m), 6.17 (1 H, br s), 6.87 (5 H, m); IR ($CHCl_3$) 3280, 2970, 1640, 1595, 1505 cm^{-1}. Anal. Calcd for $C_{13}H_{20}N_2O$: C, 70.91; H, 9.09; N, 12.73. Found: C, 70.9; H, 9.13; N, 12.74.

***N*-(2-Aminoethyl)-*N*-ethylaniline (30).** A mixture of 18.1 g (82 mmol) of **17**, 25 ml of concentrated HCl, and 50 mL of water were refluxed. After 16 h the mixture was cooled, concentrated, basified (NaOH), and extracted with chloroform. The extract was dried ($MgSO_4$), and the product **30**, 8.3 g (62% yield), was isolated by distillation; bp 118–120 °C (3 mmHg) [lit.[23] bp 120–121 °C (5 mmHg)]. Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.07 (5 H, m) (3 H, t after D_2O wash), 2.82 (2 H, m), 3.3 (4 H, m), 6.87 (5 H, m); IR (neat) 2950, 1600, 1502 cm^{-1}.

***N*-(2-(Diphenylamino)ethyl)propionamide (19).** Diphenylamine (49 g, 0.29 mol) and 1.5 g of methanesulfonic acid were heated under N_2 to 180 °C. Ethyloxazoline (30 g, 0.3 mol) was then added over a period of 5 h. After being heated for 1 h, the crude product was analyzed by liquid chromatography and the area ratios for diphenylamine, **19**, and a later eluting component were 18:76:5. A portion, 5.6 g, of the crude product, which solidified on standing at room temperature was dissolved in chloroform and washed with aqueous NaOH. The chloroform was evaporated, and the residue was recrystallized from diethyl ether to yield 3.4 g (63% yield) of **19**, mp 91.5–92 °C. Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.03 (3 H, 5), 2.0 (2 H, q), 3.37 (2 H, q), 3.72 (2 H, t), 5.75 (1 H, br s), 6.87 (10 H, m); IR ($CHCl_3$) 3010, 1660, 1587 cm^{-1}. Anal. Calcd for $C_{17}H_{20}N_2O$: C, 76.12; H, 7.46; N, 10.45. Found: C, 76.2; H, 7.56; N, 10.47.

***N*-Butyl-*N*-(2-hydroxyethyl)propionamidine (16).** Ethyloxazoline (3.0 g), 2.2 g of *n*-butylamine, and 73 mg of zinc acetate were mixed at room temperature and heated at 40 °C for 24 h in a sealed vial. The sample was then cooled to room temperature, and unreacted oxazoline and amine were removed at reduced pressure (0.1 mmHg). The residue, 2.1 g, was analyzed by ^{1}H NMR. Only a small amount of oxazoline and *n* butylamine were observed. Spectral data for the product **16**: ^{1}H NMR ($CDCl_3$) δ 1.23 (10 H, m), 1.9 (1 H, s), 2.22 (2 H, q), 3.2 (4 H, m), 3.57 (2 H, m), 5.43 (1 H, br s); IR (neat) 3400, 2920, 1625, 1575 cm^{-1}. The product is thermally unstable. Analysis by GLC showed three components: 47 area % ethyloxazoline, 39 area % *n*-butylamine, and 14 area % *N,N'*-dibutylpropionamidine (**15**).

Catalyst Screening. Catalysts were screened by heating an equimolar mixture of **7** and diethylamine with 1 mol % of the compound being screened. The mixture was heated in stainless-steel sealed tubes under N_2 at 225 °C for 19 h, cooled, and analyzed by internal standard GLC.

Comparative Reactions of Primary Amines and 2-Oxazolines. An equimolar mixture of amine and 2-oxazoline was heated for 3 h at 180 °C in a stainless-steel sealed tube. Zinc acetate was used as a catalyst at 1 mol % level.

After 3 h the mixture was cooled and analyzed by GLC. The relative area percents for the major products **11**, **12**, **13**, and **15** were determined. The structure of the products were assigned on the basis of mass spectra obtained by gas chromatography–mass spectrometry (EI (70 eV, 250 °C) and CI (ammonia, 4×10^{-5} mmHg, 200 °C)). Mass spectra, *m/e* (relative intensity): **11a** EI 100 (19), 99 (20), 86 (70), 84 (24), 57 (39), 56 (28), 44 (100), CI 173 (100), 171 (23), 155 (14), 91 (27), 74 (20); **12a** EI 154 (15), 125 (14), 111 (62), 97 (8), 69 (31), 56 (100), CI 155 (100), 153 (15); **13a** EI 100 (26), 87 (33), 86 (30), 57 (100), 44 (53), CI 147 (77), 130 (100), 100 (8), 91 (5); **15a** EI 184 (10), 155 (15), 113 (27), 86 (22), 70 (68), 56 (100), 41 (40), CI 185 (100), 112 (15); **11b** EI 100 (20), 85 (33), 72 (100), 70 (26), 57 (20), 44 (23), CI 159 (100), 157 (17), 141 (3), 91 (9); **12b** EI 140 (24), 125 (8), 97 (20), 70 (100), 69 (47), 42 (37), CI 141 (100), 139 (36); **11c** EI 157 (18), 100 (87), 86 (92), 57 (100), 44 (50), CI 173 (100), 171 (12); **12c** CI 155 (100), 153 (39); **11d** EI 128 (15), 99 (22), 86 (100), 84 (41), 57 (67), 44 (89), CI 201 (100), 199 (23), 100 (49), 86 (26), 72 (40).

Acknowledgment. We thank Dr. Patrick Langvardt for the mass spectral analysis and Dr. Henry Hennis, Dr. Dennis Klipa, and Dr. Mark Johnson for helpful discussions during the preparation of this manuscript.

Registry No. **7**, 10431-98-8; **7**·CF_3CO_2H, 93111-56-9; **8**, 63224-20-4; **10**, 100-36-7; **11a**, 93111-57-0; **11b**, 93111-59-2; **11c**, 82154-68-5; **11d**, 93111-62-7; **12a**, 93111-58-1; **12b**, 93111-60-5; **12c**, 93111-61-6; **13a**, 2955-67-1; **15a**, 93111-52-5; **16a**, 93134-27-1; **17**, 93111-53-6; **18**, 42816-34-2; **19**, 93111-54-7; **22**, 93111-55-8; **23**, 51388-00-2; **24**, 82154-67-4; **25**, 82154-69-6; **26**, 3690-53-7; **27**, 63451-19-4; **28**, 19248-13-6; **29**, 54253-60-0; **30**, 23730-69-0; Et_2NH, 109-89-7; $Zn(OAc)_2$, 557-34-6; Me-*m*-C_6H_4NHEt, 102-27-2; Me-*m*-C_6H_4NHEt·HCl, 63549-45-1; Bu_2NH, 111-92-2; PhNHEt, 103-69-5; PhNHEt·HCl, 4348-19-0; Ph_2NH, 122-39-4; CH_3SO_3H, 75-75-2; $BuNH_2$, 109-73-9; H_2WO_3, 12168-73-9; $Fe_2(SO_4)_3$, 10028-22-5; $CdCl_2$, 10108-64-2; $CoCl_2$, 7646-79-9; Me-*p*-$C_6H_4SO_3H$, 104-15-4; BF_3·Et_2O, 109-63-7; *i*-$PrNH_2$, 75-31-0; *t*-$BuNH_2$, 75-64-9; morpholine, 110-91-8; 2-phenyl-2-oxazoline, 7127-19-7; 2-undecyl-2-oxazoline, 10431-84-2; hexamethylenimine, 111-49-9; 2-*tert*-butyl-2-oxazoline, 30393-80-7.

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