Reductions with Lithium in Low Molecular Weight Amines and Ethylenediamine

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Reductions of several types of compounds with lithium and ethylenediamine using low molecular weight amines as solvent are described. In all cases 1 mol of ethylenediamine or *N*,*N*′-dimethylethylenediamine per gram-atom of lithium was used. In some cases it was beneficial to add an alcohol as a proton donor. These reaction conditions were applied to the debenzylation of *N*-benzylamide and lactams which are refractory to hydrogenolysis with hydrogen and a catalyst. *N*-Benzylpilolactam **2**, synthesized from pilocarpine hydrochloride in refluxing benzylamine, was debenzylated in good yield using 10 gram-atoms of lithium per mole (10 Li/mol) of **2** in *n*-propylamine. The debenzylation of *N*-benzyl-*N*-methyldecanoic acid amide, **4** (6 Li/mol), in *t*-butylamine/*N*,*N*′-dimethylethylenediamine gave *N*-methyldecanoic acid amide **6** in 70% yield. Alternatively, reduction of **4** (7 Li/mol) in *t*-butanol/*n*-propylamine/ethylenediamine gave *n*-decanal **12** in 36% yield. Using the same conditions, thioanisole, 1-adamantane-*p*-toluenesulfonamide, and 1-adamantane methyl *p*-toluenesulfonate were reduced with 3, 7, and 7.2 Li/mol of compound to give thiophenol (74%), adamantamine (91%), and 1-adamantane methanol (75%), respectively. In this solvent system naphthalene and 3-methyl-2-cyclohexene-1-one were reduced to isotetralin (74%) and 3-methyl cyclohexanone (quantitative) with 5 and 2.2 Li/mol of starting compound, respectively. Oximes and *O*-methyloximes were reduced to their corresponding amines using 5 and 8 Li/mol of compound, respectively. Anisole was also reduced to 1-methoxy-1,4-cyclohexadiene with 2.5 Li/mol of anisole. Undecanenitrile was reduced to undecylamine with 8.6 Li/mol. Additionally, a base-catalyzed formation of imidazolines from a nitrile and ethylenediamine was also explored.

Introduction

Alkali metal reductions of organic compounds in liquid ammonia have long been a mainstay in organic synthesis.[1] The most common of these reactions is known as the Birch reduction and consists of sodium metal in a mixture of liquid ammonia and an alkyl alcohol such as *n*-butanol or *t*-butanol. One reason this method has not seen much more use, than it already has, is that liquid ammonia is a nuisance to handle and the workup often requires a long period of waiting for the ammonia to evaporate. Several attempts have been made to minimize some of these problems. Most notably is the use of alkylamine solvents.[2,3] Extensive work in this area by Benkeser[4] and others has shown that the reaction rate decreases markedly as the solvents alkyl chain increases in length. These results have limited metal alkylamine reductions to methyl- and ethylamine. Alternatives to these volatile amines have focused on using ethylenediamine as a solvent,[5,6] which has the same nitrogen-to-carbon ratio as methylamine but is less volatile. However, reductions in ethylenediamine frequently result in over-reduction of the substrate, giving a mixture of products.[1,2]

It appeared to us that the sluggish reaction in alkyl amines might be the result of poor solvation of lithium ion. We hoped that addition of a mole of ethylenediamine per gram-atom of lithium to solvate lithium ion would increase the rate of reduction. In this paper we describe useful reaction conditions for lithium reductions using low molecular weight amines and diamines. Addition of an alcohol as a proton donor is useful in some cases.[7]

Several applications of this reducing system have been studied in this work. First and most interesting is the

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Table 1. Reaction Summary

no.	compound	cond.[a]	Li, equiv	temp, °C	time, h	yield, %	product
			Debenzylation of *N*-Benzylamides				
a	*trans*-*N*-benzylpilolactam **2**	B	1	0	4	50	*trans*-pilolactam **3**
b	*N*-benzyl-*N*-methyldecanoic acid amide **4**	B	6	−18	1	70	94% *N*-methyldacanoic acid amide **6** 5% *N*-propyldecanoic acid amide **9** 1% 2-aminoethyldecanoic acid amide **10**
c	**4**	C	6	−18, 2 h	7	75	*N*-methyldecanoic acid amide **6**
				20, 5 h		17	*N*-2-aminoethyldecaneoic acid amide **10**
d	**4**	D	6	0	1.5	70	*N*-methyldecanoic acid amide **6**
e	**4**	A	7	−18	1.5	36	*n*-decanal **8**
			Other Deprotections				
f	thioanisole **11**	B	3	0, 1 h	4	74	thiophenol **12**
				20, 3 h		6	thioanisole **11**
g	1-adamantamine *p*-toluenesulfonamide **13**	B	7	20 → 42	2	91	adamantamine **14**
h	1-adamantane methyl *p*-toluenesulfonate **16**	B	7.2	20	3	75	adamantanemethanol **17**
i	morpholine *p*-toluenesulfonamide **18**	A	9	20	4.5	38	*p*-toluenethiol **19**
			Oxime Reductions				
j	4-methycyclohexanone oxime **20**	B	5	20 → 55	1	70	93% *trans*-4-methyl-cyclohexylamine **21** 6.5% *cis*-4-methyl cyclohexylamine
k	4-methylcyclohexanone *O*-methyloxime **22**	A	8	20 → 60	1, 25 min	72	4-methylcyclohexylamine **21**
l	*n*-heptaldoxime **23**	A	5	20 → 53	2	55	*n*-heptylamine **24**
m	*n*-nonal *O*-methyloxime **25**	A	7.6	20	3	70	*n*-nonylamine **26**
			Nitrile				
n	undecanenitrile **27**	B	6	20 → 32	30 min	22	2-(*n*-decyl)imidazole **28**
o	undecanenitrile **27**	A	8.6	20 → 55	2.5	17	*n*-decane **30**
						83	undecylamine **31** (same yields with MeOH)
			Comparisons to Published Methods				
p	anisole **32**	A	2.5	−18	2	50	1-methoxy-1,4-cyclohexadiene **34**
						10	1-methoxy-1,3-cyclohexadiene **35**
q	naphthalene **33**	B	5	−6 → 20	1.5	74	1,4,5,8,-tetrahydronaphthalene **38**
r	3-methyl-2-cyclohexene-1-one **40**	B	2.2	0	1.5	100	3-methylcyclohexanone **42**

[a] Conditions: A = *n*-propylamine, ethylenediamine;B = *n*-propylamine, ethylenediamine, *t*-butanol; C = *t*-butylamine, ethylenediamine; D = *t*-butylamine, *N*,*N*′-dimethylethylenediamine.

debenzylation of *N*-benzylamides.[8,9] Other deprotections include the conversion of thioanisole to thiophenol, the reduction of *p*-toluenesulfonamides, and the cleavage of sulfonate esters. Ketoximes, aldoximes,[10] and nitriles are reduced to the corresponding amines.[2] Also presented is an interesting conversion of nitriles to imidazolines.[11] Finally this method is compared to published procedures for the reduction of anisole,[12] naphthalene,[13] and an α,*β*-unsaturated ketone.[14] The results of all reactions are outlined in Table 1. The reactions were usually carried out without any added proton sources, but in some cases added *t*-butanol was beneficial. Preliminary experiments demonstrated that the reaction is very slow in the absence of ethylenediamine which may facilitate the reaction by solvating lithium ion. At least 1 mol of ethylenediamine per gram-atom of lithium was used in all reactions.

Results and Discussion

Debenzylation of *N*-Benzylamides. The large scale preparation of *trans*-pilolactam[15] without using liquid ammonia[16] was an important objective of our work. A two-step sequence was devised that involved preparation of *trans*-*N*-benzylpilolactam **2** and subsequent cleavage of the benzyl group (Scheme 1). The first step of the synthesis was straightforward. Heating pilocarpine hydrochloride **1** with benzylamine under reflux gave *trans*-*N*-benzylpilolactam **2** as the major product. Ultimately, debenzylation of the crude *trans*-*N*-benzylpilolactam **2** gave *trans*-pilolactam **3** in 50% yield for the two steps. However, the debenzylation proved to be a problem. Hydrogenolysis with hydrogen over a catalyst was futile in accord with previous observations.[8,9] We turned our attention to carrying out the debenzylation reaction with

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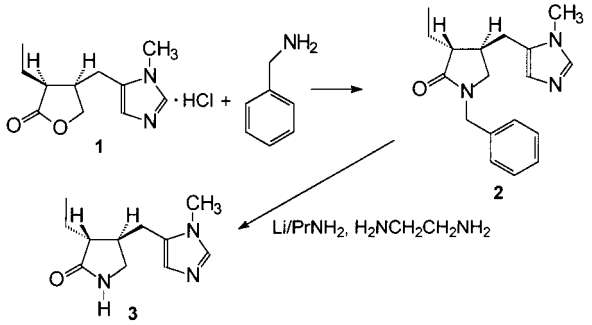
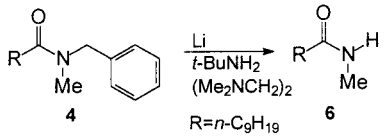
Scheme 1. Synthesis of *trans*-Pilolactam 3



lithium in a low molecular weight amine which would be easy to handle and readily recovered. The reaction of lithium with *trans*-*N*-benzylpilolactam **2** was very slow in pure *n*-propylamine. The addition of ethylenediamine greatly speeded the reaction giving a blue solution as the reaction proceeded. The addition of alcohol to the reaction mixture resulted in no useful product. Subsequent experiments showed that the formation of the amide anion protects the amide system from further reduction. In the presence of a better proton donor such as an alcohol, the free amide is formed and quickly reduced (vide infra). For the preparation of *trans*-pilolactam **3**, the best conditions employed 10 gram-atoms of lithium per mol of *trans*-*N*-benzylpiloactam **2** in *n*-propylamine with 1 mol of ethylenediamine per gram-atom of lithium. The large excess of lithium was required for reaction to reach completion. Undoubtedly, some lithium is used to reduce the toluene formed in the cleavage reaction. The reduction of the toluene may well proceed at about the same rate as debenzylation.

The reduction with lithium in *N*-propylamine/ethylenediamine of some simple *N*-benzylamides was examined to determine the scope and utility of the reaction. As expected, amides of benzoic acid undergo reduction of the benzoyl ring.[2] The *N*-benzylhexanoic acid amide suffers reduction of the benzene ring, without any debenzylation, to give a mixture of dihydro and tetrahydro derivatives.

However, reduction of *N*-benzyl-*N*-methyldecanoic acid amide **4** with lithium in *n*-propylamine afforded *N*-methyldecanoic acid amide **6** contaminated with some *N*-propyldecanoic acid amide **9** and *N*-(2-aminoethyl)-decanoic acid amide **10** (eq 1). *N*-Methyldecanoic acid



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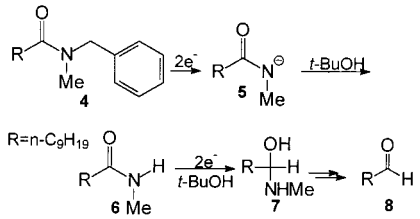
amide **6** containing 1% *N*-propyldecanoic acid amide **9** and 5% *N*-(2-aminoethyl)decanoic acid amide **10** was isolated in 70% yield by crystallization. The formation of amides derived from the solvent was surprising. The conjugate bases of the solvent amines appear to be acylated by the starting amide **4**. In an effort to prevent scrambling of the *N*-alkyl groups, the solvent was changed to *t*-butylamine and ethylenediamine. The result was that the reaction was much slower than in *n*-propylamine and debenzylation was accompanied by formation of *N*-(2-aminoethyl)decanoic acid amide **10** as a serious byproduct (19%). Using diethylamine as solvent resulted in an

Scheme 2. Reduction of Tertiary Amides in the Presence of Proton Donors



even greater amount of acylated ethylenediamine although the diethylamine did not appear to be acylated.

The observation that *t*-butylamine did not give rise to any byproducts led us to search for polyamines that would solvate lithium ion and not themselves lead to a serious side reaction. Piperazine, 1,3-diaminopropane, *N*,*N*′-dimethylethylenediamine, and tris(2-aminoethyl)-amine were examined. Piperazine is insoluble in the amine solvents and is not useful. Both 1,3-diaminopropane and tris(2-aminoethyl)amine appear to be superior to ethylenediamine for increasing the rate of reduction, but they were also acylated as serious side reactions. The secondary diamine, *N*,*N*′-dimethylethylenediamine, with *t*-butylamine as solvent, gave the best yield of pure product. With *N*-benzyl-*N*-methyldecanoic acid amide **4**, *N*-methyldecanoic acid amide **6** of greater than 99% purity was obtained in 58% yield after one crystallization. The relatively small amount of acylated *N*,*N*′-dimethylethylenediamine was washed out of the crude product with dilute acid.

A further modification of the reaction conditions was examined. The addition of alcohol to the reaction mixture resulted in further reduction of the amide (Scheme 2). In one experiment, reduction of *N*-benzyl-*N*-methyldecanoic acid amide **4** with 6 gram-atoms of lithium and 6 moles of both ethylenediamine and *t*-butanol gave *n*-decanal **8** in 36% yield on workup. Cleavage of the benzyl group must result in the conjugate base of the primary amide **5** which is stable to further reduction. Alcohol in the reaction mixture functions as a proton donor to form the free amide **6**, which is quickly reduced.[2]

The debenzylation of tertiary amides with lithium in low molecular weight amines and a polyamine is a useful alternative to classic Birch reduction conditions. The best solvent for debenzylation is *t*-butylamine and *N*,*N*′-dimethylethylenediamine which minimizes the side reactions and gives the most readily purified product.

Other Deprotections. Thioanisole **11** was reduced using 3 gram-atoms of lithium per mole of the thioether **11** in *n*-propylamine and ethylenediamine with no added alcohol. The reaction proceeded smoothly to give thiophenol **12**. The yield was 82% of material which was 91% pure by glpc (6% thioanisole **11** remaining).

Cleavage of 1-Adamantamine *p*-Toluenesulfonamide (13). Lithium in *n*-propylamine and ethylenediamine cleaved the *p*-toluenesulfonamide of 1-adamantamine to regenerate the amine **14** in 91% yield.

Cleavage of Adamantanemethyl Sulfonates. Both the *p*-toluenesulfonate **15** and methanesulfonate **16** esters of adamantane-methanol **17** suffered sulfur−oxygen cleavage to regenerate adamantanemethanol **17** in 75% and 70% yields, respectively.

Reduction of Morpholine *p*-Toluenesulfonamide (18). Under more forcing conditions a sulfonamide can be reduced to the thiol. The sulfonamide **18** was reduced

with 9 gram-atoms of lithium per mole of sulfonamide **18** in *n*-propylamine, ethylenediamine, and *t*-butanol to give a 38% yield of *p*-toluenethiol **19**.

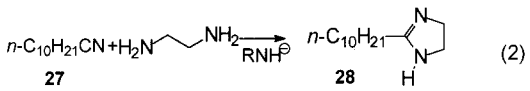
Oxime Reduction. Reduction of 4-methylcyclohexanone oxime **20** with 5 gram-atoms per mole of lithium in *n*-propylamine and ethylenediamine gave a 70% yield of the 4-methylcyclohexylamines **21**. The *trans*-isomer predominated (94:6) over the *cis*-isomer. The addition of excess *t*-butanol as a proton source had a very pronounced effect on the reaction. In the absence of any excess alcohol, the reaction is quite efficient using only a 25% excess of lithium (5 gram-atoms per mole of oxime **20**) whereas sodium and alcohol reductions of oximes require huge excess of metal.[10] The *Organic Syntheses* procedure for reducing *n*-heptaldoxime **23** with sodium and alcohol employs more than 10 gram-atoms of sodium per mole of oxime **23** and the yields are 50−70%.[10]

In comparison, reduction of *n*-heptaldoxime **23** proved more difficult than reduction of 4-methylcyclohexanone oxime **20**. Using 5 gram-atoms of lithium and 2 moles of *t*-butanol per mole of oxime **23**, the reaction gave a 55% yield of good quality *n*-heptylamine **24**. Reduction of *n*-nonanal *O*-methyloxime **25** gave a 70% yield of *n*-nonylamine **26** using 7 gram-atoms of lithium and 5 moles of *t*-butanol per mole of oxime **25**.

The reduction of 4-methylcyclohexanone *O*-methyloxime **22** gave essentially the same result as for the unsubstituted oxime **20**. However, in the case of the *O*-methyloxime **22**, the reaction proceeded better when 1 mole of *t*-butanol per gram-atom of lithium and a larger excess of lithium was used.

The oximes of benzaldehyde and acetophenone both suffered reduction of the aromatic ring with the lithium reducing system and no useful products were obtained.

Reduction of Undecanenitrile. The reaction of undecanenitrile **27** with lithium in *n*-propylamine and ethylenediamine gave an unexpected side reaction resulting in 2-(*n*-decyl)-2-imidazoline **28**. The very basic conditions resulting from partial reaction catalyze the addition of ethylenediamine to the nitrile with loss of ammonia to give the imidazoline **28** (eq 2). The reaction



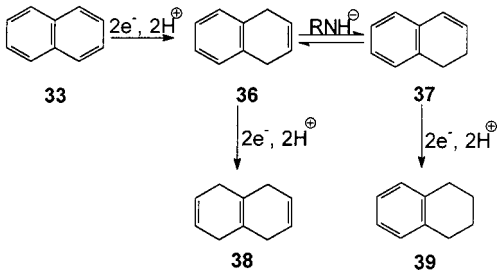
27 28 (2)

of nitriles with acid salts of ethylenediamine has long been used to prepare imidazolines.[11] However, the reaction of nitriles with ethylenediamine to give imidazolines under basic conditions appears to be a new reaction.

This process was studied further to determine its potential synthetic utility. We find that imidazoline formation takes place readily upon treating a nitrile with a solution of ethylenediamine and its conjugate base. The conjugate base of ethylenediamine was prepared by treating ethylenediamine with butyllithium in tetrahydrofuran. A full equivalent of base was required to get complete reaction in a reasonable period. Using 5 moles of ethylenediamine and 1.2 mole of butyllithium per mole of nitrile at room temperature for an hour converted undecanenitrile **27** to the corresponding imidazoline **28** in 79% yield. The same conditions with benzonitrile gave 2-phenyl-2-imidazoline **29** in 68% yield.

The conventional synthesis involves reaction of the nitrile with alcohol and hydrogen chloride to give the alkyl imidate salt which is isolated and treated with

Scheme 3. Reduction of Naphthalene

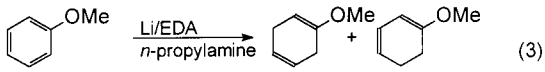


33 36 37 38 39

ethylenediamine. Alternatively, the nitrile is allowed to react directly with ethylenediamine salt which may require high temperatures and protracted reaction times.[11] Formation of imidazolines by the base-induced addition of ethylenediamine to nitriles is a useful addition to the conventional methods.

In any case, imidazoline formation seriously interfered with nitrile reduction with lithium in propylamine and ethylenediamine. We found that addition of *t*-butanol to the reaction mixture suppressed imidazoline **28** formation. Two products were obtained. Decane **30** was formed in 17% yield and *n*-undecylamine **31** accounted for the remainder of the product (83%). Conditions could not be devised to give a single clean product. A low concentration of proton donors would be expected to favor loss of cyanide with formation of *n*-decane **30**. However, imidazoline **28** formation was prominent in the absence of a proton donating alcohol. The same reasoning suggests that increasing the proton donating ability of the solvent would increase the fraction of amine obtained. Again the reaction proved refractory to changes in solvent. Replacing *t*-butanol with the better proton donor, methanol, did not change the ratio of *n*-decane **30** and undecylamine **31** formed in the reaction.

Comparisons to Published Procedures. Reduction of Anisole, Naphthalene, and 3-Methyl-2-Cyclohexen-1-one. We have compared reductions using lithium in *n*-propylamine and ethylenediamine with the *Organic Synthesis* procedures for the Birch reductions of anisole **32** (eq 3) and naphthalene **33** (Scheme 3). For



32 34 35 (3)

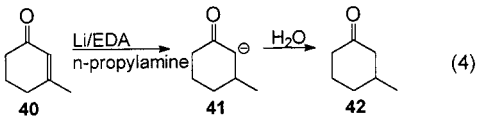
anisole **32**, the *Organic Synthesis* reaction is carried out with lithium in liquid ammonia and tetrahydrofuran with *t*-butanol as the proton source.[12] We have used the same ratio of lithium on the same scale (50 g of anisole **32**) in *n*-propylamine and ethylenediamine with *t*-butanol as the proton source. We obtained a 50% yield of 1-methoxy-1,4-cyclohexadiene **34** which contained 10% of 1-methoxy-1,3-cyclohexadiene **35** by gas chromatography and NMR. This compares favorably with the *Organic Synthesis* yield of 75% which is claimed to be pure material.

The reduction of naphthalene **33** to isotetralin **38** as described in *Organic Synthesis* is carried out by adding a solution of naphthalene **33** in ether and ethanol to a solution of sodium in liquid ammonia.[13] Some work was required in order to obtain a comparable yield of isotetralin **38** using lithium in propylamine and ethylenediamine. Adding the lithium all at once gave a satisfactory reaction on a small scale. However, the reaction was very exothermic and on a large scale was uncontrollable.

Adding lithium in portions, without cooling to −6 °C, to a solution of naphthalene **33** in propylamine and ethylenediamine containing some *t*-butanol as a proton source gave a bad mixture of products. Tetralin **39** was the major product in some cases. When a limited amount of reducing agent is present, it appears that the initially formed 1,4-dihydronaphthalene **36** isomerizes to 1,2-dihydronaphthalene **37** which is briskly reduced to tetralin **39**.

Our best procedure consisted of using 12.8 g of naphthalene **33** (the *Organic Synthesis* procedure is for 192 g of naphthalene) with 5 gram-atoms of lithium, 5 mol of ethylenediamine, and 6 mol of *t*-butanol. The lithium was added slowly keeping the reaction temperature at −6 °C. These conditions gave a 74% yield of crystalline isotetralin **38** which is to be compared to the yield from the *Organic Synthesis* procedure of 75−80%. Our results indicate that reductions of aromatic systems with lithium in *n*-propylamine and ethylenediamine are quite comparable with Birch reductions using liquid ammonia. Reactions in *n*-propylamine are certainly quicker and easier to set up and work up than those in liquid ammonia. The time taken for the ammonia to evaporate is eliminated.

Reduction of 3-methyl-2-cyclohexen-1-one **40** (eq 4) with 2.2 gram-atoms of lithium afforded 3-methylcyclohexanone **42** in essentially quantitative yield after quenching the enolate **41** with water. The *Organic Synthesis*



(4)

procedure alkylates the lithium enolate **41** with allyl bromide without isolating 3-methylcyclohexanone **42**. Nonetheless, our procedure is at least comparable to the published results.[14]

Conclusions. We have developed a modification of the Benkeser reaction that provides a useful alternative to the classic Birch reduction. This system eliminates liquid ammonia with its troublesome handling yet provides the selectivity not commonly associated with other amine solvents in this reduction. This mixed amine reaction has been demonstrated to provide an easy and convenient way to debenzylate tertiary amides, cleave sulfonamides and sulfonates, reduce oximes, and cleave thioethers. In addition nitriles can be reduced to amines or can be converted into imidazolines with base catalysis. Finally this procedure is comparable to published procedures for the reduction of naphthalene to isotetralin, anisole to 1-methoxy-1,4-cyclohexadiene, and 3-methyl-2-cyclohexene-1-one to 3-methylcyclohexanone.

Experimental Section

All reductions were carried out under nitrogen. Proton magnetic resonance spectra were measured at 60 MHz. Materials were analyzed by glpc with a thermal conductivity detector using helium as carrier gas. Column: HP-5, 10 M × 530 μm (unless otherwise noted).

***trans*-Pilolactam 3.** A solution of pilocarpine hydrochloride **1** (98 g, 0.40 mol) and 300 g (2.8 mol) of freshly distilled benzylamine was heated under reflux in a nitrogen atmosphere for 40 h. After 22 h, the reaction mixture contained about 12% of pilocarpine. The cooled reaction mixture was treated with 100 mL of 3 N sodium hydroxide, and the layers were separated. The aqueous layer was washed with two 100 mL portions of dichloromethane. The combined organic material was washed twice with water, and the dichloromethane was evaporated. The benzylamine was distilled finally at 75 °C (15 mm). The gas chromatogram of the residue, 140 g, showed 2% pilocarpine, 74% *trans*-*N*-benzylpilolactam **2**, and 10% of material eluting near the major product which might be the *cis*-isomer. The remaining material was a number of minor impurities. The crude material was used for the next step. A solution of *N*-benzylpilolactam **2** (29.7 g, 0.l mol) in 400 mL of *n*-propylamine and ethylenediamine (40 mL, 36 g, 0.59 mol) in a three-neck flask fitted with a mechanical stirrer under nitrogen was cooled to 0 °C in an ice bath. Lithium (7.0 g, 1.0 gram-atom) in small pieces was added quickly. After 20 min the internal temperature rose to 20 °C and remained there for an hour. When the temperature began to drop, the ice bath was removed. After an additional 4 h all of the lithium was gone. The reaction develops a deep maroon color. The volatile amines were evaporated under reduced pressure, and 300 mL of cold water was cautiously added to the residue (very exothermic). The aqueous solution was extracted three times with 100 mL portions of ether which removed the majority of the impurities and only a trace of the product. Three extractions with 100 mL portions of chloroform afforded 19 g of crude product after evaporation of the solvent. The gas chromatogram showed 93% of *trans*-pilolactam **3**. The crude lactam **3** was dissolved in 50 mL of acetone and filtered to removed 0.2 g of insoluble material. Another 50 mL of acetone was added, and the solution was cooled in an ice bath. A solution of *p*-toluenesulfonic acid (20 g) in 50 mL of acetone was added dropwise over 20 min to the magnetically stirred solution. Stirring was continued for another 20 min, and then the mixture was filtered to give 17.6 g (50% for two steps) of *trans*-pilolactam *p*-toluenesulfonate salt. Anal. Calcd for $C_{13}H_{17}N_3O_4S$: C, 56.97; H, 6.64; N, 11.07; S, 8.45. Found: C, 57.02; H, 6.63; N, 11.00; S, 8.42. If the *p*-toluenesulfonic acid is added rapidly to the crude base, the salt separates first as a viscous oil and a less pure product is obtained. The free base may be obtained from the salt in essentially quantitative yield by treatment with aqueous sodium hydroxide and extraction with chloroform. The product was identical to that made by the published procedure.[16]

Amides of *N*-Decanoic Acid. The *N*-benzyl-*N*-methyl[17] **4**, *N*-methyl[18] **6**, *N*-propyl[19] **9**, *N*-(2-aminoethyl)[20] **10**, and *N*-*tert*-butyl[21] amides of *n*-decanoic acid were all prepared by treating *n*-decanoyl chloride with the appropriate amine in pyridine. The amides could be purified by crystallization or distillation under reduced pressure.

Reduction of *N*-Benzyl-*N*-methyldecanoic Acid Amide 4 under Different Conditions. *n*-Propylamine and Ethylendiamine Solution. A solution of *N*-benzyl-*N*-methyldecanoic acid amide **4** (2.76 g, 10 mmol) in *n*-propylamine (30 mL) and ethylenediamine (3.6 g, 60 mmol) was cooled to −18 °C. Lithium (0.42 g, 0.06 gram-atom) was added in small pieces. The reaction mixture warmed to −8 °C and then cooled to −10 °C. After 1 h, the reaction mixture turned blue and glpc analysis of an aliquot indicated complete reaction. The reaction mixture was poured onto a mixture of 50 g of ice and 50 mL of water and extracted with ether. The combined ether extracts were washed with water and brine, and the ether was evaporated under reduced pressure to give an oil (1.8 g,). The crude product was crystallized from hexane (25 mL) with cooling to 0 °C to give 1.3 g (70%) of *N*-methyldecanamide **6**. Glpc analysis indicated *N*-methyldecanoic acid amide **6** (94%) contaminated with *N*-propyldecanoic acid amide 9 (1%) and *N*-(2-aminoethyl)decanoic acid amide **10** (5%).

***t*-Butylamine and Ethylenediamine Solution.** A solution of *N*-benzyl-*N*-methyldecanoic acid amide **4** (0.55 g, 2

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mmol) in *t*-butylamine (8 mL) and ethylenediamine (0.72 g, 12 mmol) was cooled to −18 °C, and lithium (0.084 g, 12 mmol), in small pieces, was added rapidly. After 2 h the reaction mixture was allowed to warm to room temperature. After 5 h, an aliquot of the reaction mixture showed 75% of *N*-methyldecanoic acid amide **6** and 17% of *N*-(2-aminoethyl)decanoic acid amide **10**.

***t*-Butylamine and *N,N′*-dimethylethylenediamine Solution.** A solution of *N*-benzyl-*N*-methyldecanoic acid amide **4** (2.75 g, 10 mmol) in *t*-butylamine (30 mL) and *N,N′*-dimethylethylenediamine (5.3 g, 60 mmol) was cooled in an ice bath. Lithium (0.42 g, 0.06 g-atoms) in small pieces was added at once. After 11 h, the reaction mixture was poured into a mixture of 1 M hydrochloric acid (100 mL) and ice (50 g). The crystalline product was collected by filtration and washed with water. The crude *N*-methyldecanoic acid amide **6** (1.3 g, 70%) was 91% pure by glpc. The material was stirred with 0.5 M hydrochloric acid (20 mL), filtered, and dried to give 1.14 g (61%) of product which was 96.4% pure by glpc. The crude amide was recrystallized from 7 mL of hexane and cooled to freezer temperature, to give 1.07 g (58%) of *N*-methyldecanoic acid amide **6** which was more than 99% pure by glpc.

***n*-Propylamine Solution with *t*-Butanol.** A solution of *N*-benzyl-*N*-methyldecanoic acid amide **6** (10 g, 0.036 mol) in *n*-propylamine (100 mL), ethylenediamine (13 g, 0.216 mol), and *t*-butanol (16 g, 0.216 mol) was cooled to −18 °C, and lithium (1.77 g, 0.252 mol), in small pieces was added rapidly. After 15 min, the temperature raised to 12 °C and then lowered. After another 45 min, the reaction turned blue and after another 30 min a yellow solution was obtained. The reaction mixture was poured over 75 g of crushed ice and water (75 mL). The mixture was extracted with ether, and the combined ether extracts were washed with brine. The ether was evaporated, and the residue was dissolved in THF (50 mL) and 3 N hydrochloric acid (15 mL). The solution was heated under reflux for 2 h and then cooled and diluted with brine (50 mL). The mixture was extracted with ether, and the combined ether extracts were washed with brine and filtered through 1PS filter paper. The ether was evaporated, and the residue was distilled to give 2.0 g (36%) of *n*-decanal **8**, bp 100−105 °C (15 mm).

Reduction of Thioanisole 11. Thioanisole **11** (1.24 g, 0.01 mol) in *n*-propylamine (10 mL) and ethylenediamine (1.8 g, 0.03 mol) at 0 °C was treated with lithium (0.21 g, 0.03 gram-atom). The reaction mixture turned dark blue. After 1 h the ice bath was removed, and the reaction was continued for 3 h at room temperature. The reaction mixture was then poured onto concentrated hydrochloric acid (25 mL) and ice (25 g). The mixture was extracted with ether. The ether solution was dried over sodium sulfate and evaporated to give 0.9 g (82%) of thiophenol **12** which was 91% pure by glpc (6% thioanisole **11**).

Cleavage of 1-Adamantanamine *p*-Toluenesulfonamide 13. 1-Adamantanamine *p*-toluenesulfonamide[22] **13** (4 g, 0.13 mmol), *n*-propylamine (50 mL), and ethylenediamine (6.3 g, 0.11 mol) were placed in a three-neck round-bottomed flask equipped with a mechanical stirrer, condenser, and thermometer. Lithium wire (0.64 g, 0.091 gram-atom) was added in two portions. Addition of one-half of the lithium gave a dark color and the temperature rose to 42 °C. After an hour the temperature began to fall and the remainder of the lithium was added. The blue color dissipated over 45 min, the reaction mixture was poured onto ice, and the resulting mixture was extracted with ether. The ether was washed with brine and distilled at atmospheric pressure. The residue was sublimed at 90 °C (12 mm) to give 1.79 (91%) of 1-adamantanamine **14**.

Reduction of 1-Adamantanemethyl *p*-Toluenesulfonate 15. Lithium (0.61 g, 0.087 gram-atom) was added to 1-adamantanemethyl *p*-toluenesulfonate[23] **15** (4.0 g, 0.012 mol) in *n*-propylamine (50 mL) and ethylenediamine (6 g, 0.10 mol) in a three-neck flask equipped with a mechanical stirrer, condenser, and a thermometer. Approximately half of the lithium was added at once. The remainder of the lithium was added after most of the first portion had dissolved. After 2 h, the lithium had all reacted and the reaction mixture was poured onto ice and extracted with ether. The ether was evaporated to give 1.9 g of crude 1-adamantanemethanol **17** which was sublimed under vacuum to give l.5 g (75%) of slightly yellow 1-adamantanemethanol **17**. This sample showed the same NMR spectrum as authentic material.

Reduction of 1-Adamantanemethyl Methanesulfonate 16. Reduction of a sample of 1-adamantanemethyl methanesulfonate[24] by the procedure described above gave a 70% yield of 1-adamantanemethanol **17**.

Reduction of Morpholine *p*-Toluenesulfonamide 18. Lithium (3.9 g, 0.56 gram-atom) was added in two portions to a solution of morpholine *p*-toluenesulfonamide[25] **18** (15 g, 0.062 mol) in *n*-propylamine (250 mL), ethylenediamine (37 g, 0.62 mol) and *t*-butanol (9.2 g, 0.12 mol) at room temperature. One-half of the lithium was added, and after an hour most of it had dissolved and the second portion was added. The reaction was continued to another 3.5 h and then cooled in an ice bath and treated with methanol (30 mL). Water (120 mL) was added, and the reaction mixture was evaporated under reduced pressure. Water (100 mL) was added, and the reaction mixture was concentrated under reduced pressure, cooled, and acidified with concentrated hydrochloric acid. The mixture was extracted with ether, and the combined ether extracts were washed with brine. The ether was filtered and distilled at atmospheric pressure. The residue was distilled through a short path still at 12 mm to give 2.9 g (38%) of *p*-toluenethiol **19** which was 95% pure by glpc.

Reduction of 4-Methylcyclohexanone Oxime 20. In a three-neck flask fitted with a condenser, mechanical stirrer, and a thermometer was placed a solution of 4-methylcyclohexanone oxime[26] **20** (12.7 g, 0.1 mol) in 100 mL of *n*-propylamine and ethylenediamine (30 g, 0.50 mol). Lithium (3.5 g, 0.5 gram-atom) in small pieces was added all at once. After about 25 min, the temperature rose to 55 °C and the mixture refluxed briskly. After 1 h, the reaction was blue-green and all of the lithium had reacted. The reaction mixture was mixed with 200 g of ice and extracted with ether. The ether solution was washed with 15% sodium hydroxide and brine and then dried over magnesium sulfate. The ether was evaporated, and the residue was distilled to give 7.9 g (70%) of 4-methylcyclohexylamine **21**, bp 148−150 °C (atm), which was 93.5% *trans* and 6.5% *cis* by glpc on a J&W column, CDXB, 30 M × 0.25 mm. at 100 °C.

Reduction of 4-Methylcyclohexanone *O*-Methyloxime 22. A solution of 4-methylcyclohexanone *O*-methyloxime[27] (21.15 g, 0.15 mol) in *n*-propylamine (150 mL), ethylenediamine (72 g, 1.2 mol), and *t*-butanol (89 g, 1.2 mol) was treated with lithium (8.4 g, 1.2 gram-atoms) added in two portions. Addition of half of the lithium caused a temperature rise to 62 °C and vigorous reflux. After the reaction subsided and the reaction cooled to 50 °C, the remaining lithium was added which caused another exotherm and vigorous reflux. After the blue color dissipated, the reaction mixture was poured onto 100 g of ice. The mixture was extracted with hexane; the combined hexane extracts were washed with brine and filtered through 1PS filter paper. After distillation of the hexane at atmospheric pressure, 4-methylcyclohexylamine **21** (12.6 g, 72%), bp 148−150 °C (atm), was obtained after distillation through a short Vigreux column.

Reduction of *n*-Heptanal Oxime 23. In a 1 L three-neck round-bottomed flask fitted with a condenser and a thermom-

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eter were placed *n*- heptanal oxime[28] **23** (28.5 g, 0.22 mol), *n*-propylamine (280 mL), *t*-butanol (32.6 g, 0.44 mol), and ethylenediamine (66 g, 1.1 mol). The reaction was run under nitrogen. Lithium (7.7 g, 1.1 gram-atoms) was added in two portions. Addition of one-half of the lithium raised the temperature to 53 °C. The reaction refluxed and then cooled to 40 °C over a period of 45 min. The remaining lithium was then added. The reaction resumed refluxing for a short time and then turned blue. After 1 h more the color dissipated, the reaction mixture was poured onto ice, and the resulting solution was filtered. The filtrate was treated with solid sodium hydroxide until layers formed. The organic layer was treated with solid sodium hydroxide and decanted. The organic layer was partitioned between 200 mL of hexane and 200 mL of saturated brine to remove the ethylenediamine. The brine was extracted with hexane, and the hexane solutions were combined. The hexane was distilled through a short Vigreux column leaving 19 g of crude *n*-heptylamine **24**. The original aqueous layer was extracted with ether, and the ether was distilled through a short Vigreux column. The residue from the ether was partitioned between 50 mL of hexane and 50 mL of brine. The hexane was distilled through a short Vigreux column, and the residue was combined with the material from the organic layer. Distillation through a short Vigreux column yielded 13.8 g (55%) of pure *n*-heptylamine **24**, bp 152−158 °C (atm).

Reduction of *n*-Nonanal *O*-Methyloxime 25. Lithium (1.6 g, 0.228 mol) was added in one portion to a solution of *n*-nonanal *O*-methyloxime[29] **25** (5.13 g, 0.030 mol) in *n*-propylamine (50 mL), ethylenediamine (9 g, 0.15 mol), and *t*-butanol (11 g, 0.15 mol). After 3 h, an aliquot was analyzed by glpc and no oxime was present. The reaction mixture was poured into ice−water (150 mL), and the mixture was extracted with ether. The combined ether extracts were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. Distillation of the residue afforded *n*-nonylamine **26** (3.0 g, 70%), bp 98−100 °C (20 mm). The NMR spectrum was identical with that of an authentic sample.

Reduction of Undecanenitrile 27 in *n*-Propylamine and Ethylenediamine. Lithium (0.21 g, 30 mmol) in small pieces was added to a stirred solution of undecanenitrile **27** (0.84 g, 5 mmol) in *n*-propylamine and ethylenediamine (1.0 mL, 0.89 g, 15 mmol). The temperature began to rise after 20 min and reached 32 °C after 30 min, and the reaction mixture turned blue. An aliquot of the reaction mixture showed no nitrile **27** by glpc. The reaction mixture was poured over crushed ice and extracted with ethyl acetate. After distillation of the ethyl acetate the residue deposited crystals. The crystals were collected and dried to give 2-(*n*-decyl)imidazoline **28** (0.23 g, 22%, 100% pure by glpc).

Reduction of Undecanenitrile 27 in *n*-Propylamine, Ethylenediamine, and *t*-Butanol. Lithium, (0.28 g, 40 mmol) in small pieces, was added to undecanenitrile **27** (0.775 g, 4.63 mmol) in *n*-propylamine (10 mL), ethylenediamine (1.5 g, 25 mmol), and *t*-butanol (2.22 g, 30 mmol). After 20 min, the temperature increased to 55 °C and decreased slowly. After another 2 h, the reaction mixture was poured onto a slurry of water (25 mL) and ice (25 g). The reaction mixture was extracted twice with ether. The ether extract was analyzed by glpc using ethyl benzoate as internal standard. Glpc analysis showed *n*-decane **30** in 17% yield and undecylamine **31** in 83% yield. A similar reaction using methanol in place of *t*-butanol in the same mole ratio gave the same percentages of *n*-decane **30** and undecylamine **31**.

Reaction of *n*-Undecanenitrile 27 with Ethylenediamine. A solution of ethylenediamine (9.0 g, 0.15 mol) in tetrahydrofuran (25 mL) in a three-neck flask fitted with a mechanical stirrer and a thermometer was cooled to −20 °C. A solution of *n*-butyllithium (14.4 mL of 2.5 M in hexane, 0.036 mol) was added over 5 min and after 10 min, *n*-undecanenitrile **27** (5.0 g, 0.03 mol) in tetrahydrofuran (10 mL) added over 15 min. The cooling bath was removed, and the reaction mixture was stirred at room temperature for another 30 min. An aliquot of the reaction mixture showed no *n*-undecanenitrile **27** by glpc. Water (25 mL) was added to the reaction mixture, and it was extracted with ethyl acetate. The ethyl acetate extracts were washed with brine, filtered through 1PS filter paper, and concentrated under reduced pressure to give a solid (6.5 g). The material was triturated with hexane and filtered to give 2-(*n*-decyl)-2-imidazoline **28** (5 g, 79% after drying). Glpc analysis showed a purity of 100%, mp 78−83 °C. ^{1}H NMR ($CDCl_3$) δ 5.2 (s, 1 H), 3.6 (s, 4 H), 2.3 (t, j = 7 Hz, 3 H), 1.5 (m, 16 H), 0.9 (t, j = 6, Hz,2H). Anal. Calcd for $C_{13}H_{26}N_2$: C, 74.23; H, 12.46; N, 13.32; Anal. Found: C, 73.95; H, 12.54; N, 13.22.

Synthesis of 2-Phenyl-2-imidazoline 31 from the Reaction of Benzonitrile with Ethylenediamine. A solution of ethylenediamine (15 g, 0.25 mol) in tetrahydrofuran (40 mL) in a three-neck flask fitted with a mechanical stirrer and a thermometer was cooled to −20 °C. A solution of *n*-butyllithium (24 mL of 2.5 M in hexane, 0.06 mol) added over 10 min and after 30 min, benzonitrile (5.15 g, 0.05 mol) added over 15 min. The cooling bath was removed and the reaction mixture stirred at room temperature for another hour. An aliquot of the reaction mixture showed no benzonitrile by glpc. Water (50 mL) was added to the reaction mixture which contained gummy material. The mixture was extracted with ethyl acetate. The ethyl acetate extracts were washed with brine, filtered through 1PS filter paper, and concentrated under reduced pressure to give a solid (6.1 g). The crude product crystallized from acetone (10 mL) to give 5 g (68%) of 2-phenyl-2-imidazoline **29**, which was 100% pure by glpc, mp 98−103 °C, 101 °C lit.[30]

Reduction of Anisole 32. Lithium in small pieces (8.75 g, 1.25 g-atoms) was added to a solution of anisole **32** (54 g, 0.5 mol) in *n*- propylamine (400 mL), ethylenediamine (105 g (1.75 mol), and *t*-butanol (111 g, 1.5 mol) cooled to −18 °C. The temperature raised to 12 °C and then decreased to −5 °C. After 2 h all of the lithium had reacted and the reaction mixture was diluted with 800 mL of water added slowly. The mixture was extracted with ether. The ether extracts were washed with water and brine and evaporated. The residue was distilled to give 27.5 g (50%) of 1-methoxy-1,4-cyclohexadiene **34** containing 10% 1-methoxy-1,3-cyclohexadiene **35** by glpc and NMR.

Reduction of Naphthalene 33. Lithium (3.5 g, 0.5 gram-atom) in small pieces was added portionwise to a solution, cooled to −6 °C, of naphthalene **33** (12.8 g, 0.10 mol) in *n*-propylamine (100 mL), ethylenediamine (30 g, 0.5 mol), and *t*-butanol (44.4 g, 0.6 mol). The solution warmed to 20 °C, and this temperature was maintained by addition of lithium. After 1.5 h, the reaction mixture was poured over 150 g of ice and 100 mL of water and then extracted with ether. The ether was washed with water and brine. The ether was evaporated under reduced pressure to give 12.2 g of a colorless solid which was triturated with methanol, filtered, and dried to give crude 1,4,5,8-tetrahydronaphthalene **38** which was recrystallized from methanol (50 mL) to give 9.8 g (74%) of 1,4,5,8-tetrahydronaphthalene **38** which was 93% pure by glpc.

Reduction of 3-Methyl-2-cyclohexen-1-one 40. Lithium (0.154 g, 0.022 gram-atom) was added to a solution of 3-methyl-2-cyclohexen-1-one **40** (1.1 g, 0.01 mol) in *n*-propylamine (10 mL) and ethylenediamine (1.32 g, 0.022 mol) at 0 °C. After 1.5 h, the reaction was diluted with water (25 mL) and extracted with ether. The ether was washed with brine and evaporated under reduced pressure to give a quantitative yield of 3-methylcyclohexanone **42** which showed by NMR spectrum and glpc to be identical with that of authentic material.

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