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CYCLIZATION OF AMINYL RADICALS GENERATED BY ANODIC OXIDATION OF LITHIUM ALKENYLAMIDES. STEREO- AND REGIOSELECTIVE SYNTHESIS OF cis-1-ALKYL-2,5-DISUBSTITUTED PYRROLIDINES

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Abstract — Neutral aminyl radicals (**3**) generated by anodic oxidation of lithium alkenylamides (**2**) were found to undergo a stereo- and regioselective cyclization to give cis-1-alkyl-2,5-disubstituted pyrrolidines (**5c - 5h**) in moderate yields. The cis stereochemistry of **5c - 5h** was confirmed by comparison with the corresponding trans-1-alkyl-2,5-disubstituted pyrrolidines which were prepared by aminomercuration of **1c - 1h**. The structure of trans-1,2-dimethyl-5-phenylpyrrolidine (**17**) was established by an X-ray crystallographic analysis of its ammonium bromide **21**. Various aminyl radicals examined in this study were found to combine exclusively with the internal carbon of their double bond to give a five- (**5a - 5h**) or six-membered ring (**13**). No product arising from the cyclization is obtained from N-methyl-1-phenylbut-3-enylamine (**14**).

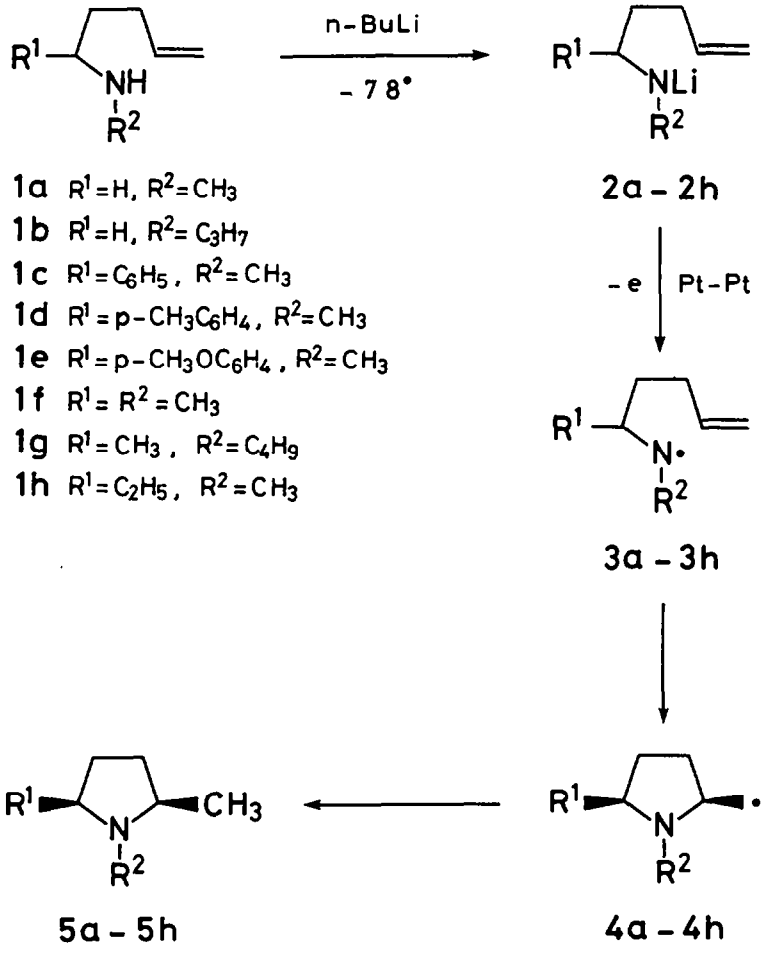
Ever since cyclization of a hex-5-enyl radical has been found to give a five-membered carbocycle regioslectively,[1] carbon radical cyclization has been extensively studied from both mechanistic[2-4] as well as synthetic viewpoints.[5] These investigations have demonstrated that the carbon radical cyclizations are useful for the preparation of some of the five-membered alicyclic and even for some heterocyclic compounds.[6] In contrast, little attention has been paid to the cyclization of neutral nitrogen-centered radicals (aminyl radicals),[7] although protonated aminyl radicals (aminium radicals) or aminyl radicals complexed to metal ion are known to undergo facile cyclization.[8] In most of the reported cyclizations of neutral aminyl radicals, N-chloroalkenylamine has been used as a precursor of the radical and, hence, cyclization often gives a product containing a chlorine atom.[7] It has been reported that aminyl radicals can be generated by means of an anodic oxidation of lithium alkylamides[9] in the same way as we have generated the carbon radicals by the electrolysis of lithium ester enolates.[10] We have already reported

a preliminary result that the neutral aminyl radicals generated by anodic oxidation of lithium alkenylamides underwent a stereoselective cyclization to give cis-1-methyl-2,5-disubstituted pyrrolidines **5c - 5f** and **5h**.[11] We describe here a full detailed result of these cyclizations and also describe a regiochemistry and a stereochemistry of the aminyl radical cyclizations. This cyclization provides a new method for the stereoselective synthesis of cis-1-methyl-2,5-disubstituted pyrrolidines.

RESULTS AND DISCUSSION

Our synthesis of cis-1-methyl-2,5-disubstituted pyrrolidines by means of cyclization of the aminyl radicals is outlined in Scheme I. Treatment of alkenylamines **1** with butyllithium at -78 °C readily affords lithium alkenylamides **2**. Anodic oxidation of **2** at the platinum anode generates the aminyl radicals **3** which undergo cyclization to give the substituted pyrrolidines **5**.

Cyclization of N-alkylpent-4-enylamine. In our first attempt, N-methylpent-4-enylamine (**1a**) was converted into **2a**. Electrolysis of **2a** at a constant current of 25 mA/cm^2 in a 30:1 mixture of tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPA) containing 0.25M lithium perchlorate at -10 °C led to a 70% conversion of **1a** and gave **5a** in a 6% yield together with a large amount of



Scheme I.

Table I. Cyclization of **1a - 1h** by anodic oxidation of **2a - 2h**[a]

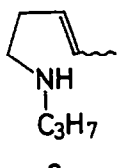
Amine	Temp. °C	Product	Yield of 5 %[b]	Recovered 1 %[b]
1a	-10	**5a**	6	30
1b	-50	**5b**	7	66
1c	-10	**5c**	52	29
1c	-50	**5c**	41	48
1d	-10	**5d**	48	44
1e	-10	**5e**	46	50
1f	-10	**5f**	31	9
1f	-50	**5f**	20	20
1g	-78	**5g**	2	50
1h	-10	**5h**	34	4
1h	-78	**5h**	26	10

[a]Electrolysis of 0.06M **2a - 2h** in a 30:1 mixture of THF-HMPA containing 0.25M $LiClO_4$ was carried out at a platinum anode by the use of a divided cell. Electricity passed was 1.2 Faradays per mol of **2a - 2h**. [b]Determined by GLC analysis using an internal standard method. Yields are based on **2** employed.

an unidentified complex mixture (Table I). Similarly, lithiation of N-propylpent-4-enylamine (**1b**) to **2b** followed by electrolysis at -50 °C led to 34% conversion of **1b** and gave **5b** in a 7% yield. The electrolysis of **2b** in the same solvent containing 0.1M KI instead of $LiClO_4$, however, gave N-propylpent-3-enylamine **6** (20%) due to an isomerization of the terminal double bond of **1b** along with an 8% yield of **5b**.

In contrast to the successful cyclization of **1a** and **1b**, the stable aminyl radical with a more bulky phenyl group generated from N-phenylpent-4-enylamine (**7**) failed to cyclize to give a pyrrolidine derivative. The starting amine **7** was recovered unchanged.

No product arising from the cyclization of the aminyl radical **3b**, which was generated by a hydrogen abstraction of **1b** with tert-butoxy radical, was detected probably because of its slow cyclization.[12] However, our results showed that the neutral aminyl radicals such as **3a** and **3b** generated by means of anodic oxidation undergo the cyclization to give pyrrolidines **5a** and **5b**, albeit in low yields.



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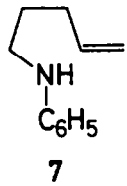

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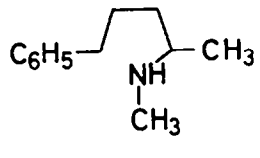

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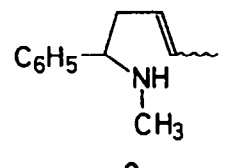

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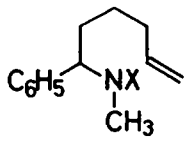

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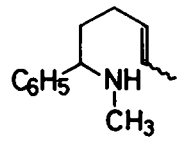
11 X = Li



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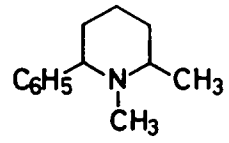

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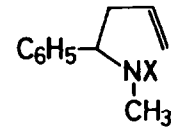


14 X = H
15 X = Li

Chart I.

Cyclization of 1-substituted N-alkylpent-4-enylamine. Synthesis of cis-N-alkyl-2,5-disubstituted pyrrolidines. Although the aminyl radicals generated from the lithium amides of **1a** and **1b** cyclized with only low efficiency to give pyrrolidines **5a** and **5b**, it was considered that the N-alkylpent-4-enylamines with a substituent attached to the C-1 may give better yields of cyclized products. The rate of the cyclization is expected to be faster in these substrates due to gauche interactions between the C-1 and the C-2 groups.[13]

1-Substituted N-alkylpent-4-enylamines **1c-1h** were prepared as shown in the sequence outlined in Scheme II. The results of the anodic oxidation of lithium N-methyl-1-phenylpent-4-enylamide (**2c**) under various conditions are summarized in Table II. As expected, 1,2-dimethyl-5-phenyl pyrrolidine (**5c**), a product of the cyclization, was obtained as a sole product when electrolysis of 0.06M **2c** in THF-HMPA was conducted in an anode chamber by the use of a divided cell at -10~-50 °C (entries 4-9). Spectral results of **5c** were in agreement with the assigned formula. The configuration of the 2,5-disubstituents was ascertained to be cis and this will be discussed later.

The best yield (52%) of pyrrolidine **5c** was achieved when a mixture of THF-HMPA containing 0.25M lithium perchlorate was conducted at a constant current of 25 mA/cm^2 with platinum anode by the use of a divided cell at -10 °C. The electrolysis at -50 °C gave **5c** in a lower yield. Electrolysis of **2c** with unseparated anode and chathode chambers gave pyrrolidine **5c** with accompanying formation of the byproducts **8** and **9** (entries 1 and 2). Spectral analysis revealed that the structures of byproducts **8** and **9** were N-methyl-1-methyl-4-phenylbutylamine and N-methyl-1-phenylpent-3-enylamine. Amine **8** may be formed by the reductive cleavage of **5c**. It was observed that the yield of **5c** diminished when electricity of more than 1.2 Faradays was passed. This indicates a decomposition of **5c** at the anode, owing to prolonged oxidation (entries 8 and 9). The isomer **9** may be formed by the removal of the allylic hydrogen of terminal olefin **1c** with the strong base **2c**. The formation of the byproducts such as **6** and **9** due to isomerization were observed when the

Table II. Anodic oxidation of **2c** under various conditions[a]

Entry	Supporting electrolyte (M)	Current density mA/cm^2	Temp. °C	Recovered **1c** %[b]	Yield, %[b]		
					5c	**8**	**9**
1[c]	———	15-5	0	5	9	6	33
2[c]	0.1M KI	25	0	4	22	14	17
3	———	5	0	7	29	0	23
4	0.1M KI	25-5	-50	58	10	0	trace
5	0.25M $LiClO_4$	25-18	-50	48	41	0	0
6	0.25M $LiClO_4$	25	-10	29	52	0	0
7[d]	0.25M $LiClO_4$	25-18	-50	52	41	0	0
8[e]	0.25M $LiClO_4$	25	-10	21	25	0	0
9[f]	0.25M $LiClO_4$	25	-50	14	8	0	0
10[g]	0.1M $LiClO_4$	25	0	67	0	0	0

[a]Electrolysis of 0.06M **2c** in THF-HMPA was carried out at a platinum anode by the use of a divided cell. Electricity passed was 1.2 Faradays per mol of **2c**. [b]Determined by GLC analysis using an internal standard method. Yields are based on **1c** employed. [c]Undivided cell was used for electrolysis. [d]Concentration of **2c** was 0.13M. [e]Electricity passed was 1.7 Faradays per mol of **2c**. [f]Electricity passed was 3.0 Faradays per mol of **2c**. [g]Instead of **2c**, the amine **1c** was directly electrolyzed in methanol solution.

electrolysis was carried out at 0 °C in the presence of potassium iodide as an electrolyte. The completion of the electrolysis under these conditions required a longer time owing to a smaller current density (entries 1-4). No pyrrolidine **5** was obtained by a direct anodic oxidation of amine **1c** itself.

The formation of lithium salts of N-methyl-1-(4-methylphenyl)pent-4-enylamine (**1d**), N-methyl-1-(4-methoxyphenyl)pent-4-enylamine (**1e**), N-methyl-1-methylpent-4-enylamine (**1f**), and N-methyl-1-ethylpent-4-enylamine (**1h**) followed by the similar anodic oxidation in THF-HMPA containing 0.25M $LiClO_4$ at a platinum anode by the use of a divided cell also gave cis-1-methyl-2,5-disubstituted pyrrolidines **5d**, **5e**, **5f**, and **5h** in fair yields. The results are shown in Table I. Throughout the above cyclizations, no trans 2,5-disubstituted pyrrolidine isomers were obtained. The cylization is therefore highly stereoselective. Only a very poor yield of pyrrolidine **5g** was obtained by the anodic oxidation of the lithium salt of unsaturated amine **1g** with a bulky butyl substituent attached to the nitrogen.

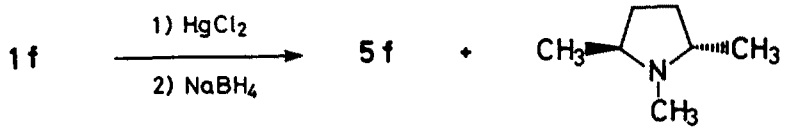
Regiochemistry of aminyl radical cyclization. It has been well established that the cyclization of hex-5-enyl and related carbon centered radicals takes place regioselectively in an exo mode to afford a five-membered ring.[1-5] Our results clearly indicate that the intramolecular combination of neutral aminyl radicals generated from N-alkylpent-4-enylamines takes place regioselectively in an exo mode. The total absence of piperidine derivatives as a result of an endo cyclization was confirmed by GLC analysis of the products obtained by anodic oxidation of the lithium salts of unsaturated amines **1a-1h**.

We further studied that the regioselectivity of the cyclization of aminyl radicals by examining the products arising from the cyclization of aminyl radicals generated from N-alkylhex-5-enylamine and N-alkylbut-3-enylamine. Lithiation of N-methyl-1-phenylhex-5-enylamine (**10**) followed by the electrolysis in HMPA-THF containing 0.25M $LiClO_4$ at -50 °C led mostly to the regeneration of the starting amine **10**, although a small amount of a product **13** was detected by GC-mass spectrometry. Product **13** may be identified to 1,2-dimethyl-6-phenylpiperidine (**13**) on the basis of its mass spectrum.[14] Electrolysis of **11** in THF-HMPA containing 0.1M KI as an electrolyte at 0 °C, on the other hand, gave N-methyl-1-phenylhex-4-enylamine (**12**) in a 72% yield and a trace amount of the starting amine **10**. The isomeric unsaturated amine **12** is most likely to be formed by the intra- or intermolecular removal of the allylic hydrogen of **11** by the negatively charged nitrogen of **11**. Isomer **12** was obtained in a 93% yield when lithium salt **11** was stirred for 2 h at 0 °C followed by hydrolysis.

Finally, lithiation of N-methyl-1-phenylbut-3-enylamine (**14**) and electrolysis of the lithium amide **15** at -50 °C gave no cyclization product. The starting amine **14** (43%) was recovered together with an intractable high boiling mixture.

Stereochemistry of N-alkyl-2,5-disubstituted pyrrolidines obtained by electrochemical cyclization. The stereochemistry of **5c-5h** was established as follows. A catalytic hydrogenation of 2,5-dimethylpyrrole over a platinum catalyst followed by N-methylation gave a single 1,2,5-trimethylpyrrolidine; this was identical to the **5f** obtained by electrolysis. This result can be taken as a supporting evidence that the 2,5-dimethyl groups of **5f** are cis oriented. It has been reported that the intramolecular aminomercuration of N-propyl-1-methylpent-4-enylamine followed by the reduction with sodium borohydride gives a mixture of 2,5-dimethylpyrrolidines and 2-methylpiperidines.[15] No assignment was made of the stereochemistry of the 2,5-disubstituents of the pyrrolidines. We therefore subjected alkenylamine **1f** to this intramolecular aminomercuration in order to prepare

pyrrolidine **5f** and its trans isomer (**16**) for comparison with the pyrrolidine formed by electrolysis. Treatment of **1f** with mercury(II) chloride in THF-H_2O followed by reduction with sodium borohydride gave two isomeric pyrrolidines in 10% and 49% yields and the pyrrolidine formed in a lower yield with a shorter retention time in GLC was identical with **5f** obtained by electrolysis. The two substituents in **16** obtained in a higher yield must therefore be trans oriented. The similar intramolecular amination of **1c** also gave two isomeric pyrrolidines in 17% and 35% yields together with recovered **1c**. The pyrrolidine with a shorter retention time in GLC formed in a 17% yield was identical with **5c** obtained by the electrolysis.



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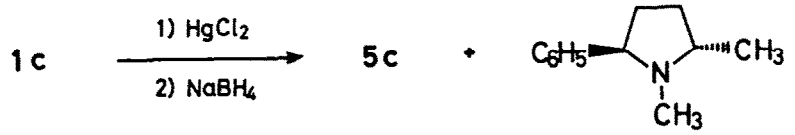
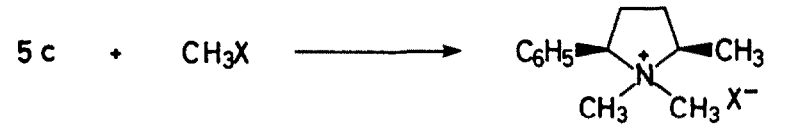


17

Although pyrrolidine **5c** gave only its oily quaternary ammonium iodide **18** and bromide **19**, the isomeric pyrrolidine **17** formed in a 35% yield gave a crystalline quaternary ammonium iodide **20** or bromide **21**. The configuration of the 2,5-disubstituents was then established by X-ray crystallographic analysis of the quaternary ammonium bromide **21**. The molecular structure of **21** is shown in Fig. 1. The two substituents attached to the C-2 and C-5 of **17** are trans oriented. On the basis of this result the phenyl and the methyl groups of **5c** are established to be cis oriented.



18 X = I
19 X = Br

20 X = I
21 X = Br

Intramolecular aminomercurations of other amines **1d**, **1e**, **1g**, and **1h** similarly gave pairs of two isomeric pyrrolidines.[16] The pyrrolidines formed in much lower yields with shorter retention times in GLC were always identical with the pyrrolidines **5d**, **5e**, **5g**, and **5h** obtained by electrolysis. We therefore assume that all the 2,5-disubstituted pyrrolidines obtained either in lower yields in the amino-

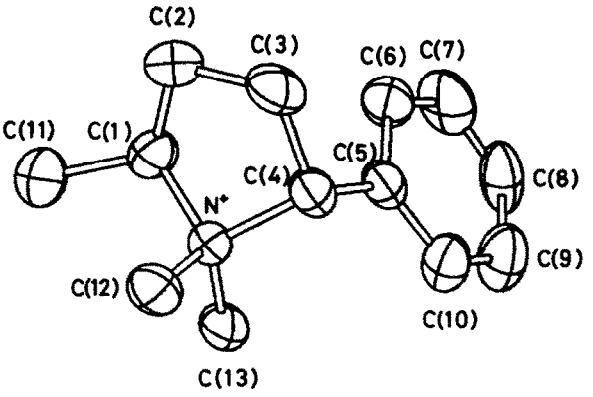


Figure 1. The molecular structure of cis-1,2-dimethyl-5-phenylpyrrolidine quaternary ammonium bromide (**21**) and crystallographic numbering scheme.

mercuration reaction or by electrolysis of lithium salts of the 1-substituted N-alkylpent-4-enylamines have cis 2,5-disubstituents. It should be noted that although Lattes and his colleagues reported the formation of significant amounts of piperidine derivatives together with pyrrolidine derivatives from their intramolecular aminomercuration , no appreciable amounts of piperidine derivatives were obtained in our aminomercuration.

The present experiments have established that the neutral aminyl radicals generated by the anodic oxidation of the lithium salts of 1-substituted N-alkylpent-4-enylamine cyclize in a highly regio- and stereoselective manner to give cis-1-alkyl-2,5-disubstituted pyrrolidines. It is worth noting that this stereochemical outcome of the cyclization of the aminyl radicals is not parallel to the results of the cyclization of 2-substituted hex-5-enyl carbon radicals which is known to take place in a non-stereoselective manner; the cyclization of 2-substituted hex-5-enyl radicals gives cis- and trans-1,3-disubstituted cyclopentanes in a ratio of 0.56:1[13] and that of 1-substituted hex-5-enyl radicals affords cis- and trans-1,2-disubstituted cyclopentanes in a ratio of 2.3:1.[17] More experiments must be carried out before any firm explanation can be made of the stereochemistry of the cyclization that leads to the exclusive formation of the cis isomers in the present electrolysis. The observed high stereoselectivity in the cyclization, however, might be attributable to the adsorption of the radical species on their unhindered face by the electrode surface.

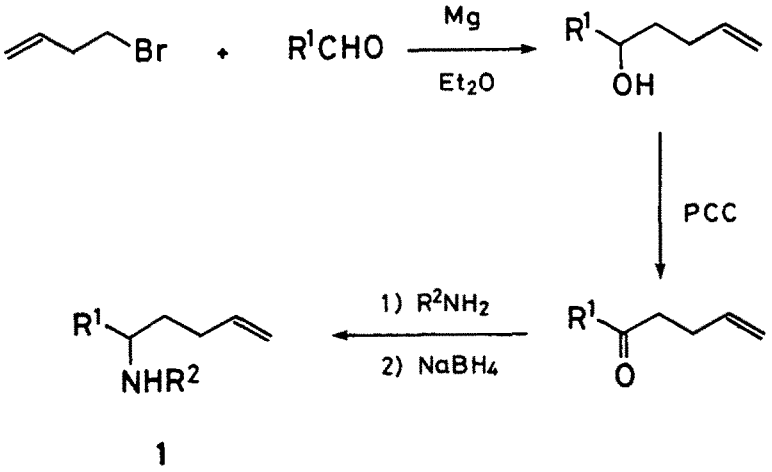
EXPERIMENTAL

General method. THF was dried over sodium benzophenone ketyl and distilled before use. HMPA was dried over calcium hydride and distilled at a reduced pressure under nitrogen before use. IR spectra were determined with a Hitachi Model 285 spectrometer. ^{1}H NMR spectra were measured with a Hitachi R-90H (90 MHz), a JEOL FX200 (200 MHz) (Faculty of Pharmaceutical Science of this University), or a Varian XL200 spectrometer (200 MHz) (solvent $CDCl_3$, $SiMe_4$ as an internal reference). ^{13}C NMR spectra were measured with a JEOL FX100 (25 MHz) (solvent $CDCl_3$, $SiMe_4$ as an internal reference). Mass spectra were obtained with a JEOL JMS-D300 mass spectrometer. Quantitative GLC analyses were carried out with a Hitachi 063 instrument by an internal standard method.

Preparations of alkenylamines. N-Methyl- (**1a**) and N-propylpent-4-enylamine (**1b**) were prepared in yields of 71% and 85% from 1-bromo-4-pentene and the appropriate amines according to the published method.[18] 1-Bromo-4-pentene[19] was prepared by bromination of 4-penten-1-ol[20] obtained by the reaction of tetrahydrofurfuryl chloride with sodium metal. **1a**: bp 110-112°C; n_D^{20} 1.4281; IR (neat) 3300, 3090, 1640, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.69 (s, 1H), 1.49 (qi, 2H), 2.06 (q, 2H), 2.34 (s, 3H), 2.50 (t, 2H), 4.8-5.1 (m, 2H), 5.5-6.0 (m, 1H). **1b**: bp 92-95°C (107 mmHg); n_D^{20} 1.4340; IR (neat) 3270, 3070, 1640, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3H), 1.23 (s, 1H), 1.2-1.7 (m, 4H), 2.10 (q, 2H), 2.58 (t, 2H), 2.63 (t, 2H), 4.8-5.1 (m, 2H), 5.6-6.1 (m, 1H).

1-Substituted N-alkylpent-4-enylamines **1c-1h** were prepared according to the following procedure (Scheme II) unless stated otherwise. A Grignard reagent from magnesium (0.17 mol) and 1-bromo-3-butene (0.17 mol) in diethyl ether (150 mL) was added to aldehyde (0.17 mol) dissolved in diethyl ether (40 mL) and the mixture was heated under reflux for 1 h. The usual work-up of the solution gave the corresponding alcohols (30-67%). To pyridinium chlorochromate (PCC, 0.11 mol) in dichloromethane (100 mL) was added the alcohol (0.074 mol) dissolved in dichloromethane (10 mL) and the mixture was heated under reflux for 3 h. After the mixture had been passed through a short silica gel column, a distillation of the products at a reduced pressure gave the unsaturated ketones (70-90%). A mixture of the ketone (0.064 mol), an excess of methylamine, and magnesium sulfate (20 g) in dry diethyl ether (70 mL) was heated in an autoclave at 70-80°C for 17-22 h. After magnesium sulfate was removed by filtration, a product imine dissolved in anhydrous methanol (20 mL) was treated with sodium borohydride (0.053 mol) at room temperature. After evaporation of most of the solvent, the desired amine was extracted with diethyl ether and the solution was washed with water and saturated sodium chloride solution successively; it was then dried over anhydrous magnesium sulfate. Distillation gave **1c-1h** (50-76%).

N-Methyl-1-phenylpent-4-enylamine (**1c**). This amine was prepared by the two different methods: (a), the reaction of 1-bromo-3-butene (0.22 mol) and N-benzylidenemethylamine (0.067 mol) according to the procedure of Moffett,[21] by which distillation gave 3.28 g of **1c** (19 mmol, 28%); (b), the Grignard reaction. Bp 123-126°C (16 mmHg); n_D^{20} 1.5153; IR (neat) 3330, 3090, 3065, 3030, 1640, 1135,



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Scheme II.

995, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (s, 1H), 1.6-2.2 (m, 4H), 2.17 (s, 3H), 3.39 (t, 1H), 4.8-5.1 (m, 2H), 5.5-6.0 (m, 1H), 7.2 (s, 5H); mass spectrum m/z 175 (M^+, 0.5), 120 (100), 91 (7), 42 (28). Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, N, 7.99. Found: C, 82.30; H, 9.85; N, 7.86.

N-Methyl-1-(4-methylphenyl)pent-4-enylamine (**1d**). Bp 77-78°C (0.7 mmHg); n_D^{20} 1.5130; IR (neat) 3300, 3075, 1640, 1135, 995, 910, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (s, 1H), 1.5-2.1 (m, 4H), 2.26 (s, 3H), 2.33 (s, 3H), 3.41 (t, 1H), 4.8-5.1 (m, 2H), 5.5-6.0 (m, 1H), 7.13 (s, 2H); mass spectrum m/z 189 (M^+, 0.7), 135 (10), 134 (100), 105 (5), 91 (5). Anal. Calcd for $C_{13}H_{19}N$: m/z 189.1518. Found: m/z 189.1543.

N-Methyl-1-(4-methoxyphenyl)pent-4-enylamine (**1e**). Bp 99-100°C (0.15 mmHg); n_D^{20} 1.5209; IR (neat) 3320, 3070, 1640, 1610, 1505, 1240, 1035, 995, 908, 828 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (s, 1H), 1.6-2.1 (m, 4H), 2.25 (s, 3H), 3.40 (t, 1H), 3.80 (s. 3H), 4.8-5.1 (m, 2H), 5.5-6.0 (m, 1H), 6.86 (d, 2H), 7.18 (d, 2H); mass spectrum m/z 205 (M^+, 2), 174 (7), 151 (11), 150 (100), 121 (6). Anal. Calcd for $C_{13}H_{19}NO$: m/z 205.1467. Found: m/z 205.1470.

N-Methyl-1-methylpent-4-enylamine (**1f**). A mixture of 5-hexen-2-one (0.102 mol), diethyl ether containing excess methylamine (60 mL), and magnesium sulfate (10 g) in an autoclave was heated at 70-80°C for 22 h. After the magnesium sulfate was filtered off, the mixture was stirred overnight in the presence of sodium borohydride (0.079 mol) and anhydrous methanol (200 mL). The usual work-up and distillation gave **1f** (55%): bp 130-131°C; n_D^{20} 1.4308; IR (neat) 3400, 3075, 1640, 1160, 995, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (d, 3H), 1.22 (s, 1H), 1.2-1.6 (m, 2H), 2.11 (q, 2H), 2.40 (s, 3H), 2.3-2.7 (m, 1H), 4.8-5.1 (m, 2H), 5.5-6.1 (m, 1H); mass spectrum m/z 113 (M^+, 0.6), 98 (2), 58 (100). Anal. Calcd for $C_7H_{15}N$: m/z 113.1204. Found: m/z 113.1211.

N-Butyl-1-methylpent-4-enylamine (**1g**). A mixture of 5-hexen-2-one (0.15 mol), butylamine (1.37 mol), and magnesium sulfate (15 g) was heated under reflux for 3.5 h. After magnesium sulfate had been filtered off, the mixture was reduced with sodium borohydride (0.2 mol) in anhydrous methanol (150 mL). The usual work-up and distillation gave 15.1 g of **1g** (97 mmol; 67%): bp 82-84°C (15 mmHg); n_D^{20} 1.4345; IR (neat) 3350, 3070, 1640, 1160, 995, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, 3H), 0.98 (d, 3H), 1.30 (s, 1H), 1.0-1.7 (m, 6H), 2.03 (q, 2H), 2.56 (m, 3H), 4.8-5.1 (m, 2H), 5.5-6.0 (m, 1H); mass spectrum m/z 155 (M^+, 2), 140 (2), 100 (100), 58 (9), 43 (33). Anal. Calcd for $C_{10}H_{21}N$: m/z 155.1672. Found: m/z 155.1647.

N-Methyl-1-ethylpent-4-enylamine (**1h**). Bp 78-80°C (50 mmHg); n_D^{20} 1.4350; IR (neat) 3300, 3075, 1640, 995, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H), 1.17 (s, 1H), 1.3-1.7 (m, 4H), 2.11 (q, 2H), 2.40 (s, 3H), 2.3-2.6 (m, 1H), 4.9-5.2 (m, 2H), 5.6-6.1 (m, 1H); mass spectrum m/z 127 (M^+, 1.3), 98 (25), 72 (100), 57 (10), 42 (9). Anal. Calcd for $C_8H_{17}N$: m/z 127.1358. Found: m/z 127.1352.

N-Phenylpent-4-enylamine (**7**). This amine was prepared from aniline (0.2 mol) and 1-bromo-4-pentene (0.05 mol) according to the published method.[22] Distillation of the reaction mixture gave 5.6 g of **7** (0.035 mol; 70%): bp 127.5°C (13 mmHg); n_D^{20} 1.5454; IR (neat) 3415, 3050, 3020, 1640, 1600, 1500, 995, 915 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73 (qi, 2H), 2.20 (q, 2H), 3.16 (t, 2H), 3.50 (bs, 1H), 4.9-5.2 (m, 2H), 5.6-6.2 (m, 1H), 6.67 (m, 3H), 7.18 (m, 2H); mass spectrum m/z 161 (M^+, 18), 106 (100), 77 (17). Anal. Calcd for $C_{11}H_{15}N$: m/z 161.1202. Found: m/z 161.1202.

N-Methyl-1-phenylhex-5-enylamine (**10**). This amine was prepared from 1-bromo-4-pentene and N-benzylidenemethylamine.[21] A solution of N-benzylidenemethylamine (0.0615 mol) in 20 mL of anhydrous diethyl ether was slowly added to the Grignard reagent prepared from 1-bromo-4-pentene (0.25 mol) and magnesium (0.24 g atom). After being stirred at reflux temperature for 2 h, the mixture was worked up as usual. Distillation gave 3.1 g of **10** (0.0164 mol; 27%): bp 89-92°C (1 mmHg);

n_D^{20} 1.5113; IR (neat) 3300, 3070, 3025, 1640, 1135, 915, 765, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (s, 1H), 1.3 (m, 2H), 1.58 (q, 2H), 1.99 (q, 2H), 2.20 (s, 3H), 3.39 (t, 1H), 4.8-5.1 (m, 2H), 5.4-6.0 (m, 1H), 7.27 (s, 5H); mass spectrum m/z 189 (M^+, 4), 174 (1.2), 120 (100), 104 (9). Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.20; H, 10.17; N, 7.25.

N-Methyl-1-phenylbut-3-enylamine (**14**). This amine was prepared from allyl bromide and N-benzylidenemethylamine in the same way as **10**. The reaction of N-benzylidenemethylamine (0.20 mol) with the Grignard reagent of allyl bromide (0.80 mol) gave 25 g of **14** (0.155 mol; 78%): bp 41-43°C (0.2 mmHg); n_D^{20} 1.5146; IR (neat) 3350, 3080, 3030, 1643, 1135, 920, 765, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 (s, 1H), 2.27 (s, 3H), 2.41 (t, 2H), 3.56 (t, 1H), 4.95-5.25 (m, 2H), 5.5-6.0 (m, 1H), 7.36 (s, 5H); mass spectrum m/z 161 (M^+, 20), 146 (17), 120 (93), 84 (100). Anal. Calcd for $C_{11}H_{15}N$: C, 81.93; H, 9.38; N, 8.69. Found: C, 81.71; H, 9.30; N, 8.55.

General procedure for aminyl radical cyclizations. The typical procedure for lithiation and anodic oxidation is to add butyllithium (2.1 mmol) dropwise to unsaturated amines **1** (2.0 mmol) in 10 mL of THF at -78°C followed by stirring at -10°C for 30 min; this afforded the corresponding lithium salts **2** in a good yield. Lithium amides **2** in a mixed solution of THF (30 mL) and HMPA (1 mL) containing 0.1-0.25 M lithium perchlorate or potassium iodide as a supporting electrolyte was transferred to an anode chamber and the mixture was electrolyzed at -10~-78°C under a nitrogen atmosphere using a platinum plate anode (2×2 cm^2). Electricity of 1.2-1.4 Faradays per mol of **1** was passed. During the electrolyses, a precipitation of lithium metal on a cathode was observed. After electrolysis, the anolyte was dissolved in 150 mL of diethyl ether and the solution was washed with water, saturated sodium chloride solution, and dried over magnesium sulfate. The usual work-up of the solution gave a product mixture which was subjected to distillation followed by preparative GLC or column chromatography. Spectral data of the products thus obtained are given below.

1,2-Dimethylpyrrolidine (**5a**): bp 84-87°C; ^1H NMR ($CDCl_3$) δ 1.00 (d, 3H, J=5.8 Hz), 1.3-1.9 (m, 6H), 2.16 (s, 3H), 2.90 (m, 1H), mass spectrum m/z 99 (M^+, 17), 98 (11), 84 (100), 71 (16), 56 (34).

2-Methyl-1-propylpyrrolidine (**5b**): bp 133-138°C; n_D^{20} 1.4344; IR (neat) 1455, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3H), 1.06 (d, 3H, J= 5.8 Hz), 1.2-2.3 (m, 9H), 2.5-2.9 (m, 1H), 3.0-3.3 (m, 1H); mass spectrum m/z 127 (M^+, 12), 112 (57), 98 (100), 84 (11), 70 (25), 69 (18). Calcd for $C_8H_{17}N$: m/z 127.1358. Found: m/z 127.1355.

cis-1,2-Dimethyl-5-phenylpyrrolidine (**5c**): n_D^{20} 1.5152; IR (neat) 3030, 3055, 1600, 1495, 760, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (d, 3H, J=5.9 Hz, C^2-CH_3), 1.6 (m, 2H), 2.0 (m, 2H), 2.09 (s, 3H, N-CH_3), 2.34 (m, 1H, J=5.9 and 7.5 Hz, C^2H), 3.15 (t, 1H, J=8.1 Hz, C^5H), 7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.4 (q, C^2-CH_3), 31.8 and 32.9 (t, t, C^3, C^4), 38.4 (q, NCH_3), 62.2 (d, C^2), 72.4 (d, C^5), 126.5, 127.2, 127.9, and 143.9 (phenyl). Irradiation of the doublet at δ 1.19 ppm caused the multiplet at δ 2.34 ppm to collapse to a triplet centered at δ 2.34 (J=7.5 Hz). Mass spectrum m/z 175 (M^+, 3), 160 (100), 98 (21), 91 (4), 42 (6). Anal. Calcd for $C_{12}H_{17}N$: m/z 175.1361. Found: m/z 175.1376.

cis-1,2-Dimethyl-5-(4-methylphenyl)pyrrolidine (**5d**): n_D^{20} 1.5126; IR (neat) 1510, 1200, 815 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (d, 3H, J=5.9 Hz, C^2-CH_3), 1.6 (m, 2H), 1.9 (m, 2H), 2.08 (s, 3H, NCH_3), 2.33 (s, 3H, $C_6H_4CH_3$), 2.3 (m, 1H, C^2H), 3.10 (t, 1H, J=8.0 Hz, C^5H), 7.12 (d, 2H), 7.24 (d, 2H); mass spectrum m/z 189 (M^+, 16), 188 (12), 174 (100), 143 (14), 98 (34), 42 (14). Anal. Calcd for $C_{13}H_{19}N$: m/z 189.1517. Found: m/z 189.1509. Product **5d** was readily isolated in a 38% yield by

column chromatography (alumina; hexane-diethyl ether 20:1).

cis-1,2-Dimethyl-5-(4-methoxyphenyl)pyrrolidine (**5e**): n_D^{20} 1.5168; IR (neat) 1610, 1510, 1245, 1045, 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (d, 3H, J=5.9 Hz, C^2-CH_3), 1.4-1.7 (m, 2H), 1.96 (m, 2H), 2.07 (s, 3H, N-CH_3), 2.29 (m, 1H, -C^2H), 3.09 (dd, 1H, J=7.8 and 8.3 Hz, -C^5H), 3.80 (s, 3H, OCH_3), 6.85 (d, 2H), 7.26 (d, 2H); mass spectrum m/z 205 (M^+, 20), 204 (14), 191 (14), 190 (100), 98 (26), 42 (12). Decoupling of the doublet due to the methyl protons at δ 1.17 caused the multiplet at δ 2.29 to collapse to a triplet (J=8.0 Hz). Anal. Calcd for $C_{13}H_{19}NO$: m/z 205.1467. Found: m/z 205.1472.

cis-1,2,5-Trimethylpyrrolidine (**5f**): IR (neat) 1450, 1215 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (d, 6H, J=5.9 Hz, C^2-CH_3, C^5-CH_3), 1.36 (m, 2H), 1.82 (m, 2H), 2.15 (m, 2H, C^2H, C^5H), 2.22 (s, 3H, N-CH_3); mass spectrum m/z 113 (M^+, 12), 98 (100), 70 (6), 56 (6). Anal. Calcd for $C_7H_{15}N$: m/z 113.1202. Found: m/z 113.1175.

cis-1-Butyl-2,5-dimethylpyrrolidine (**5g**): n_D^{20} 1.4372; IR (neat) 1460, 1205 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, 3H), 1.10 (d, 6H, J=6.2 Hz, C^2-CH_3, C^5-CH_3), 1.36 (m, 6H), 1.75 (m, 2H), 2.55 (m, 4H, N-CH_2, C^2H, C^5H); mass spectrum m/z 155 (M^+, 12), 140 (64), 112 (100), 84 (14). Anal. Calcd for $C_{10}H_{21}N$: m/z 155.1673. Found: m/z 155.1661.

cis-5-Ethyl-1,2-dimethylpyrrolidine (**5h**): IR (neat) 1460, 1210 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H), 1.10 (d, 3H, J=5.9 Hz, C^5-CH_3), 1.34 (m, 2H), 1.7-1.0 (m, 4H), 1.97 (m, 1H, C^2H), 2.15 (m, 1H, C^5H), 2.23 (s, 3H, N-CH_3); mass spectrum m/z 127 (M^+, 2), 112 (3), 98 (100). Decoupling of the doublet at δ 1.10 causes the multiplet at δ 2.15 to collapse to a doublet of doublet (J=7.5 and 6.5 Hz). Anal. Calcd for $C_8H_{17}N$: m/z 127.1362. Found: m/z 127.1374.

N-Propylpent-3-enylamine (**6**): IR (neat) 3300, 3020, 1660, 1135, 970, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, 3H), 1.4-1.7 (m, 6H), 2.27 (q, 2H), 2.63 (q, 4H), 5.5 (m, 2H); mass spectrum m/z 127 (M^+, 2), 98 (12), 72 (100), 43 (20). Calcd for $C_8H_{17}N$: m/z 127.1358. Found: m/z 127.1351.

N-Methyl-1-methyl-4-phenylbutylamine (**8**): IR (neat) 3300, 3020, 1600, 1495, 845, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (d, 3H), 1.44 (s, 1H), 1.2-1.8 (m, 4H), 2.37 (s, 3H), 2.5-2.8 (m, 2H, 1H), 7.2 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.8 (q, C^1-CH_3), 27.9 (t, C^3), 33.9 (q, N-CH_3), 36.1 (t, C^2), 36.5 (t, C^4), 54.8 (d, C^1), 125.7, 128.3, 128.4, and 142.5 (phenyl); mass spectrum m/z 177 (M^+, 0.4), 162 (0.9), 58 (100). Anal. Calcd for $C_{12}H_{19}N$: m/z 177.1516. Found: m/z 177.1516.

N-Methyl-1-phenylpent-3-enylamine (**9**): IR (neat) 3320, 3030, 1660, 1605, 1595, 1135, 765, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.55 and 1.80 (d, d, 3H), 1.61 (m, 2H), 1.94 (m, 2H), 2.26 (s, 3H), 3.52 (t, 1H), 5.4 (m, 2H), 7.27 (s, 5H); mass spectrum m/z 175 (M^+, 0.2), 120 (100), 91 (5), 42 (21). Anal. Calcd for $C_{12}H_{17}N$: m/z 175.1361. Found: m/z 175.1385.

N-Methyl-1-phenylhex-4-enylamine (**12**): IR (neat) 3320, 3070, 3025, 1660, 1135, 970, 765, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (s, 1H), 1.55 and 1.80 (each d, 3H), 1.61 (m, 2H), 1.90 (m, 2H), 2.22 (s, 3H), 3.41 (t, 1H), 5.15-5.6 (m, 2H), 7.28 (s, 5H); mass spectrum m/z 189 (M^+, 0.4), 120 (100), 42 (4). Anal. Calcd for $C_{13}H_{19}N$: m/z 189.1517. Found: m/z 189.1542.

Preparation of cis-1,2,5-trimethylpyrrolidine (**5f**) by catalytic hydrogenation. 2,5-Dimethylpyrrole (1.0 g, 10.5 mmol) was hydrogenated over PtO_2 (50 mg) in 20 mL of acetic acid according to the method of Robles.[23] Hydrogenation was carried out overnight at 70°C at a pressure of 3-4 Kg/cm^2. After the removal of PtO_2, the mixture was treated with 100 mL of 20% potassium hydroxide solution and the organic materials were extracted with diethyl ether. The usual work-up and distillation gave 0.15 g of cis-2,5-dimethylpyrrolidine (15%): bp 115-118°C; n_D^{20} 1.4419; IR (neat) 3250, 1150, 1015 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (d, 6H, J=6.3 Hz), 1.28

(m, 2H), 1.57 (s, 1H), 1.87 (m, 2H), 3.11 (m, 2H); mass spectrum m/z 99 (M^+, 4), 98 (21), 84 (100), 71 (16). Anal. Calcd for $C_6H_{13}N$: m/z 99.1046. Found: m/z 99.1041.

Butyllithium (1.3 mmol) in hexane was added at -78°c to cis-2,5-dimethylpyrrolidine (1.3 mmol) in 10 mL of dry diethyl ether and the mixture was stirred for 0.5 h at 0°C. After the solution was again cooled to -78°C, methyl iodide (1.3 mmol) was added and the solution was stirred for 1 h at -78°C and then overnight at r.t. The usual work-up and preparative GLC (OV-17) afforded cis-1,2,5-trimethylpyrrolidine (**5f**) as a single product. Its spectral data were identical to those of **5f** obtained by the anodic oxidation of **2f**. Anal. (authentic sample) Calcd for $C_7H_{15}N$: m/z 113.1204. Found: m/z 113.1196.

Aminomercuration of N-methyl-1-phenylpent-4-enylamine (**1c**). Mercury(II) chloride (2.36 g, 8.7 mmol) was added to a stirred solution of amine **1c** (1.42 g, 8.1 mmol) in 30 mL of THF and water (1:1). The mixture was stirred for 24 h under a nitrogen atmosphere. Sodium borohydride (350 mg, 9.2 mmol) was added to the mixture and it was stirred at r.t. for 3 h. After a saturated Na_2CO_3 solution had been added to the mixture, it was stirred for an additional 4 h. After most of THF had been evaporated, the residue was diluted with diethyl ether and washed with brine. The ethereal layer was dried over $MgSO_4$, filtered, and concentrated. Distillation gave a fraction boiling at 103-106°C (16 mmHg), which showed three peaks upon GLC analysis. The three fractions due to these peaks were isolated by a preparative GLC (CW 20M).

The first fraction was identical with cis-pyrrolidine **5c**. The second fraction was identified to be trans 1,2-dimethyl-5-phenylpyrrolidine (**17**): IR (neat) 3060, 3025, 1600, 1195, 755, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (d, 3H, J=6.9 Hz, C^2-CH_3), 1.55 (m, 1H), 1.8 (m, 1H), 2.13 (s, 3H, N-CH_3), 2.27 (m, 2H), 3.37 (m, 1H, J=6.9, 6.6, and 3.2 Hz, C^2H), 3.69 (dd, 1H, J=8.0 and 6.7 Hz, C^5H), 7.29 (s, 5H); ^{13}C NMR ($CDCl_3$) δ 14.8 (q, C^2-CH_3), 31.8 and 33.2 (t, t, C^3 or C^4), 35.0 (q, N-CH_3), 58.3 (d, C^2), 66.9 (d, C^5), 126.8, 127.6, 128.2, and 144.1 (phenyl); mass spectrum m/z 175 (M^+, 3), 160 (100), 98 (25). Anal. Calcd for $C_{12}H_{17}N$: m/z 175.1359. Found: m/z 175.1349. Decoupling of the doublet due to the methyl protons at δ 1.04 caused the multiplet at δ 3.37 to collapse to a double-doublet (J=3.2 and 6.6 Hz). The third fraction was identified to be the starting amine **1c**. A quantitative analysis by GLC showed that the aminomercuration of **1c** gave **5c**, **17**, and the recovered **1c** in yields of 17%, 35%, and 34%.

Aminomercuration of N-methyl-1-methylpent-4-enylamine (**1f**). Amine **1f** (0.45 g; 4 mmol) was treated with mercury(II) chloride (1.15 g; 4.2 mmol) in the same way as **1c**. GLC analysis of the reaction mixture showed the presence of two fractions, each of which was isolated by a preparative GLC.

The first fraction was identical with the authentic sample of **5f**. The second fraction was identified as trans-1,2,4-trimethylpyrrolidine (**16**): n_D^{20} 1.4345; IR (neat) 1215, 1125 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (d, 6H, J=6.4 Hz, C^2-CH_3, C^5-CH_3), 1.37 (m, 2H), 2.00 (m, 2H), 2.30 (s, 3H, N-CH_3), 2.97 (m, 2H, C^2H, C^5H); mass spectrum m/z 113 (M^+, 18), 98 (100), 85 (13), 71 (20), 70 (17), 57 (48). Anal. Calcd for $C_7H_{15}N$: m/z 113.1202. Found: m/z 113.1169. Quantitative analysis by GLC showed that the aminomercuration of **1f** gave **5f** and **16** in the yields of 10% and 49%.

Preparations of quarternary ammonium iodides **18** and **20** of pyrrolidines **5c** and **17**. A large excess of methyl iodide was added to amine **5c** (46 mg; 0.26 mmol) in 5 mL of diethyl ether and the mixture was stirred at r.t. for 2 h. Evaporation of

the solvent and the unreacted methyl iodide gave cis-1,1,2-trimethyl-5-phenylpyrrolidinium iodide (**18**) as an oil (62 mg; 0.20 mmol): ^{1}H NMR ($CDCl_3$) δ 1.53 (d, 3H, J=6.8 Hz), 2.09 (m, 1H), 2.55 (m, 3H), 2.61 (s, 3H), 3.18 (s, 3H), 4.53 (m, 1H), 5.66 (dd, 1H, J=7.3 and 11.7 Hz), 7.48 (m, 3H), 7.71 (m, 2H). Decoupling of the doublet due to the methyl proton at δ 1.53 caused the multiplet at δ 4.53 to collapse to a doublet of a doublet (J=7.4 and 10.2 Hz). Attempts to induce crystallization of the oil were unsuccessful.

Similarly, trans amine **17** (148 mg, 0.85 mmol) was treated with a large excess of methyl iodide. Evaporation of the solvent and an excess of methyl iodide gave a product (174 mg, 0.55 mmol). Recrystallization from acetone-diethyl ether gave trans-1,1,2-trimethyl-5-phenylpyrrolidinium iodide (**20**) as white needles: mp 151-152°C. IR (Nujol) 1265, 925, 780, 765, 705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.64 (d, 3H, J=6.8 Hz), 2.18 (m, 1H), 2.65 (m, 3H), 2.86 (m, 3H), 3.30 (s, 3H), 4.18 (m, 1H), 5.33 (t, 1H, J=7.8 Hz), 7.48 (m, 3H), 7.75 (m, 2H). Decoupling of the doublet due to the methyl protons at δ 1.64 caused the multiplet at δ 4.18 to collapse to a triplet (J=7.8 Hz).

Preparations of quarternary ammonium bromides **19** and **21** of pyrrolidines **5c** and **17**. Methyl bromide generated from sodium bromide (30 mg), methanol (20 mL), and sulfuric acid (14 mL) was bubbled in a solution of **5c** (92 mg, 0.53 mmol) in 5 mL of diethyl ether for a period of 3 h. Evaporation of the solvent gave **19** as an yellow oil. Attempts to induce crystallization failed.

Similarly, **17** (235 mg, 1.24 mmol) in 10 mL of diethyl ether was treated with methyl bromide. Evaporation of diethyl ether and methyl bromide gave an oil, which in turn gave crystals (147 mg, 0.55 mmol) by dilution with hexane. Repeated recrystallization of the crystals from acetone-benzene gave trans-1,1,2-trimethyl-5-phenylpyrrolidinium bromide (**21**) as monoclinic crystals: mp 174-176°C; IR (Nujol) 1265, 980, 915, 780, 760, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.61 (d, 3H, J=6.9 Hz), 2.17 (m, 1H), 2.64 (m, 1H), 2.90 (s, 3H), 3.38 (s, 3H), 4.12 (m, 1H), 5.45 (dd, 1H, J=6.8 and 7.8 Hz), 7.47 (m, 3H), 7.75 (m, 2H). Decoupling of the doublet due to the methyl protons at δ 1.61 caused the multiplet at δ 4.12 to collapse to a triplet (J=7.9 Hz). Anal. Calcd for $C_{13}H_{20}NBr$: C, 57.79; H, 7.46; N, 5.18; Br, 29.57. Found: C, 57.54; H, 7.45; N, 5.31; Br, 29.52.

X-Ray crystallographic analysis of **21**. A colorless single crystal with dimensions of about 0.5×0.4×0.4 mm was used for data collection. The crystal data were as follows: $C_{13}H_{20}NBr$, mol wt 270.21, monoclinic, space group $P2_1/c$, a=13.105(4), b=10.111(4), c=10.769(4) Å, β=112.72(2)°, z=4, d_c=1.364 g cm^{-3}. The cell dimensions and diffraction intensities were measured on a Rigaku four-circle diffractometer at the High-Brilliance X-ray Laboratory of Hokkaido University, using graphite-monochromated Mo Kα radiation (λ=0.71073 Å). The θ-2θ scanning technique was applied at a θ scan rate of 4° min^{-1}; the background was counted for 15 s at each end of the scan range. Three standard reflections, measured at intervals of every 100 reflections, showed no significant decrease in intensity during the course of data collection. The intensities were corrected for the Lorentz and polarization factors, but not for the absorption of the extinction effect. In the range of 2θ values up to 53°, 1884 selected for the structure factors above the 3σ(F) level were selected for the structure determination.

The structure was solved by the Monte Carlo direct method,[24] and refined by the block-diagonal least-squares method with anisotropic temperature factors. After all the hydrogen atoms had been located in a difference Fourier map, further full-matrix least-squares refinements were carried out including the hydrogen atoms. The final R value was 0.045. A perspective view of the molecule in the

Table III. Bond distances (A) and bond angles (°)

C(1)-C(2)	1.514(9)	C(2)-C(1)-C(11)	115.6(5)
C(1)-C(11)	1.531(9)	C(2)-C(1)-N	103.2(5)
C(1)-N	1.530(7)	C(11)-C(1)-N	112.8(5)
C(2)-C(3)	1.530(10)	C(1)-C(2)-C(3)	106.6(5)
C(3)-C(4)	1.510(7)	C(2)-C(3)-C(4)	106.8(5)
C(4)-C(5)	1.510(7)	C(3)-C(4)-C(5)	116.6(4)
C(4)-N	1.551(7)	C(3)-C(4)-N	102.0(4)
C(5)-C(6)	1.393(9)	C(5)-C(4)-N	112.2(5)
C(5)-C(10)	1.384(7)	C(4)-C(5)-C(6)	122.8(5)
C(6)-C(7)	1.373(11)	C(4)-C(5)-C(10)	119.9(5)
C(7)-C(8)	1.361(10)	C(6)-C(5)-C(10)	117.3(5)
C(8)-C(9)	1.372(13)	C(5)-C(6)-C(7)	120.3(6)
C(9)-C(10)	1.387(10)	C(6)-C(7)-C(8)	122.2(8)
C(12)-N	1.509(8)	C(7)-C(8)-C(9)	118.5(7)
C(13)-N	1.496(7)	C(8)-C(9)-C(10)	120.3(7)
		C(5)-C(10)-C(9)	121.4(7)
		C(1)-N-C(4)	102.4(4)
		C(1)-N-C(12)	112.3(4)
		C(1)-N-C(13)	112.6(5)
		C(4)-N-C(12)	108.3(5)
		C(4)-N-C(13)	114.1(4)
		C(12)-N-C(13)	107.2(4)

crystal is presented in Figure I. Bond distances and bond angles are shown in Table III.[25]

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REFERENCES AND NOTES

(1) R. C. Lamb, P. W. Ayers, and M. K. Toney, J. Amer. Chem. Soc., 85, 3483 (1963).

(2) M. Julia, Pure Appl. Chem., 40, 553 (1974); M. Julia, Acc. Chem. Res., 4, 386 (1971).

(3) A. L. J. Beckwith, Tetrahedron, 37, 3073 (1981); A. L. J. Beckwith and K. U. Ingold, "Rearrangements in Ground and Excited States"; P. de Mayo, Ed., Academic Press, New York, p. 161 (1980).

(4) J-M. Surzur, "Reactive Intermediates"; R. A. Abramovitch, Ed., Prenum Press, New York, Vol. 2, p. 121 (1982).

(5) A. Y. Mohammed and D. L. J. Clive, J. C. S. Chem. Commun., 588 (1986); L. Set, D. R. Cheshire, and D. L. J. Clive, Ibid., 1205 (1985); A. G. Angoh and D. L. J. Clive, Ibid., 941 (1985); G. Stork and M. Kahn, J. Amer. Chem. Soc., 107, 500 (1985); G. Stork and P. M. Sher, Ibid., 105, 6765 (1983); G. Stork and R. Mook, Jr., Ibid., 105, 3720 (1983); A. L. J. Beckwith, D. M. O'Shea, and D. H. Roberts, J. C. S. Chem. Commun., 1445 (1983); O. Moriya, M. Okawara, and Y. Ueno, Chem. Lett., 1437 (1984); Y. Ueno, K. Chino, M. Watanabe, O. Moriya, and M. Okawara, J. Amer. Chem. Soc., 104, 5564 (1982); H. Nishiyama, T. Kitajima, M. Matsumoto, and K. Itoh, J. Org. Chem., 49, 2298 (1984); M. Ladlow and G. Pattenden, Tetrahedron Lett., 25, 4317 (1984); H. Nagashima, H. Wakamatsu, K.

Itoh, Y. Tomo, and J. Tsuji, Ibid., 24, 2395 (1983); M. Okabe, M. Abe, and M. Tada, J. Org. Chem., 47, 1775 (1982); S. K. Pradhan, J. N. Kolhe, and J. S. Mistry, Tetrahedron Lett., 23, 4481 (1982); N. N. Marinovic and H. Ramanathan, Ibid., 24, 1871 (1983); T. Shono, I. Nishiguchi, H. Ohmizu, and M. Mitani, J. Amer. Chem. Soc., 100, 545 (1978); T. Shono, I. Nishiguchi, and H. Ohmizu, Chem. Lett., 1233 (1976); E. J. Corey and S. G. Pyne, Tetrahedron Lett., 24, 2821 (1983).

(6) D. J. Hart and H-C. Hung, Tetrahedron Lett., 26, 3749 (1985); D. A. Burnett, J-K. Choi, D. J. Hart, and Y-M. Tsai, J. Amer. Chem. Soc., 106, 8201 (1984); D. J. Hart and Y-M. Tsai, Ibid., 106, 8209 (1984); Idem., Ibid., 104, 1430 (1982); A. L. J. Beckwith and D. R. Boate, Ibid., 26, 1761 (1985); A. Padwa, H. Nimmesgern, and G. S. K. Wong, J. Org. Chem., 50, 5620 (1985); S. Kano, Y. Yuasa, K. Asami, and S. Shibuya, Chem. Lett., 735 (1986); M. Pezechk, A. P. Brunetiere, and J. Y. Lallemand, Tetrahedron Lett., 27, 3715 (1986); G. E. Keck and E. J. Enholm, Ibid., 26, 3311 (1985).

(7) J. M. Surzur, L. Stella, and P. Tordo, Tetrahedron Lett., 3107 (1970); J. M. Surzur, L. Stella, and R. Nouguier, Ibid., 903 (1971); J-L. Stein, L. Stella, and J. M. Surzur, Ibid., 21, 287 (1980); J. W. Bestable, J. D. Hollson, and W. D. Riddell, J. C. S. Perkin Trans. I, 2205 (1972).

(8) For recent reviews, see L. Stella, Angew. Chem., Int. Ed. Engl., 22, 337 (1983); M. B. Gasc, A. Lattes, and J. J. Perie, Tetrahedron, 39, 703 (1983).

(9) R. Bauer and H. Wendt, Angew. Chem., Int. Ed. Engl., 17, 202 (1978); T. Fuchigami, T. Sato, and T. Nonaka, J. Org. Chem., 51, 366 (1986).

(10) M. Tokuda, T. Shigei, and M. Itoh, Chem. Lett., 621 (1975).

(11) M. Tokuda, Y. Yamada, T. Takagi, H. Suginome, and A. Furusaki, Tetrahedron Lett., 26, 6085 (1985).

(12) Y. Maeda and K. U. Ingold, J. Amer. Chem. Soc., 102, 328 (1980).

(13) A. L. J. Beckwith and T. Lawrence, J. C. S. Perkin Trans. II, 1535 (1979); A. L. J. Beckwith, T. Lawrence, and A. K. Serelis, J. C. S. Chem. Commun., 484 (1980).

(14) Mass spectrum of **13** showed the presence of an ion at m/z 174 as the base peak and a series of ions at m/z 189 (M^+, 6%), 117 (40%), and 112 (24%). Of other possible products which have the parent peak at m/z 189, the starting amine **10** and N-methyl-1-phenylhex-4-enylamine (**12**) showed the ions at m/z 174 (M^+-Me) with only 1% intensity, while a seven-membered nitrogen heterocycle arising from the endo-cyclization of **10** is not able to give an ion at m/z 174 as the base peak.

(15) J. J. Perie, J. P. Laval, J. Roussel, and A. Lattes, Tetrahedron, 28, 675 (1972).

(16) Details of the intramolecular aminomercurations of **5c-5h** will be published elsewhere.

(17) A. L. J. Beckwith, I. Blair, and G. Phillipon, J. Amer. Chem. Soc., 96, 1613 (1974); M. A. M. Bradney, A. D. Forbes, and J. Wood, J. C. S. Perkin Trans. II, 1655 (1973).

(18) R. A. Perry, S. C. Chem, B. C. Menon, K. Hanaya, and Y. L. Chow, Can. J. Chem., 54, 2385 (1976).

(19) R. P. Linstead and H. N. Rydon, J Chem. Soc., 1998 (1934).

(20) L. A. Brooks and H. R. Snyder, "Organic Syntheses"; Wiley: New York, Collect. Vol. 3, p. 698 (1955).

(21) R. B. Moffett, "Organic Synthesis"; Wiley: New York, Collect. Vol. 4, p. 605 (1963).

(22) F. G. Willson and T. S. Wheeler, "Organic Syntheses"; Wiley: New York, Collect. Vol. 1, p. 102 (1932).

(23) H. V. Robles, Rec. Trav. Chim., 58, 111 (1939).

(24) A. Furusaki, Acta Crystallogr., A35, 220 (1979).
(25) The atomic coordinates and thermal parameters for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this paper.