Synthesis of Heterocyclic Compounds Using Amidines as Their Ene-1,1-diamine Tautomers. II. Synthesis of 2,3-Dihydropyridine, 3,4-Dihydropyridine and 3,4-Dihydropyrrol-2-one Derivatives by the Reaction of Amidines with α,β-Unsaturated Carbonyl Compounds

Kunio Ito*, Yoshiko Kizuka and Shogo Ihara

Department of Applied Chemistry, Faculty of Engineering,
Toyo University,
Kujirai, Kawagoe, Saitama 350-8585, Japan
e-mail: chemito@eng.toyo.ac.jp

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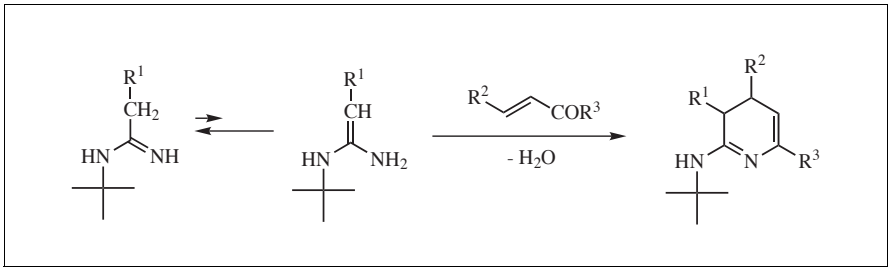

N-t-Butylacetamidines **1** on heating with methyl vinyl ketone, acrolein or crotonaldehyde gave the 2,3-dihydropyridine derivatives **4**, **5** or **6** *via N*-alkylation of the acetamidines **1**. Reaction of amidines **1** with phenyl 1-propenyl ketone, benzalacetone or chalcone gave 3,4-dihydropyridine derivatives **8**, **9** or **10**. These were obtained by *C*-alkylation, achieved by Michael addition of the acetamidines **1** as their *N,C*-tautomers ene-1,1-diamines **1'** to *α,β*-unsaturated carbonyl compounds, and subsequent cyclodehydration of adducts. Reaction of **1** with ethyl 3-benzoylacrylate gave 3,4-dihydropyrrol-2-one derivatives **13**.

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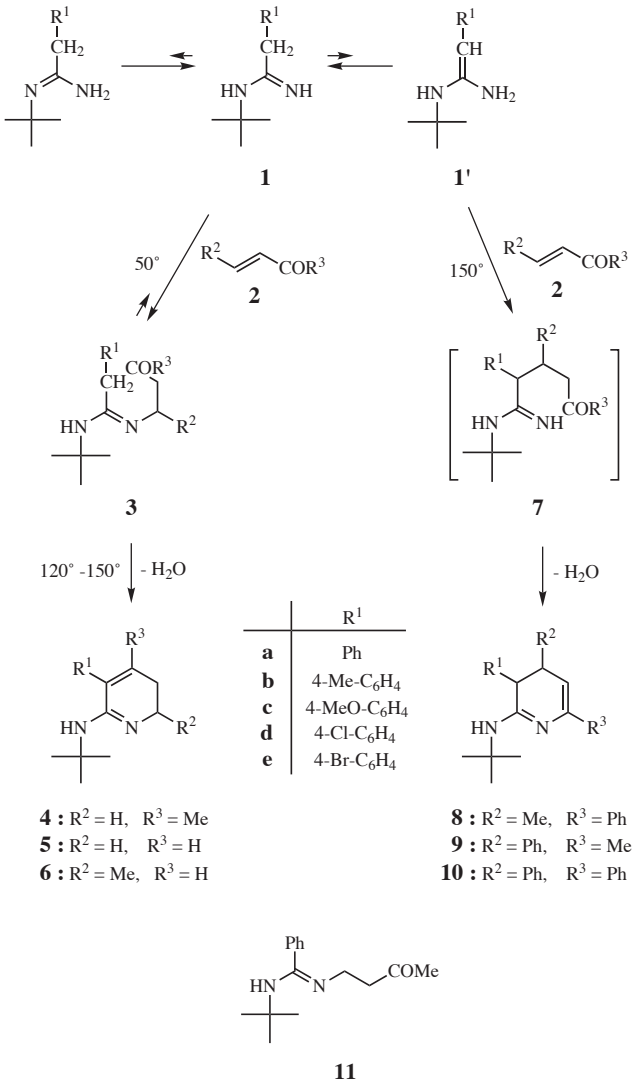
In a previous paper, we reported convenient syntheses for 4,5-dihydro-3*H*-pyridin-2-one, 3,4-dihydro-pyrrol-2-one and 1,3-dihydropyrrol-2-one derivatives by reaction of monosubstituted amidines with *α,β*-unsaturated esters [1]. Until that time, there had been no reports for *C*-alkylation in which the monosubstituted amidines react *via* the *N,C*-tautomer ene-1,1-diamines. Thus, we considered that further study on *C*-alkylation of monosubstituted amidines was worthwhile. In the present study, we extended our study to the reaction of *α,β*-unsaturated carbonyl compounds.

N-t-Butylbenzylamidine (**1a**) was heated with methyl vinyl ketone (**2** (R^2=H, R^3=Me)) at 50° for 3 hours in monoglyme. After the solvent and low-boiling materials were removed under reduced pressure, *N*-alkylated product **3a** (R^2=H, R^3=Me), formed by addition of the amidine **1a** *via* the *N,N'*-tautomer azaenamine, was obtained in 95 % yield. A diglyme solution of the obtained **3a** (R^2=H, R^3=Me) was heated in a 120° oil bath for 2 hours. The solvent was removed and the residue was vacuum distilled to obtain the 2,3-dihydropyridine derivative **4a** (57 %) as well as **1a** which was formed by the reverse reaction of **3a**. The product **4a** was crystallized by standing at room temperature. The structure of **4a** was confirmed by elemental analysis, spectroscopic measurements and X-ray crystal structural analysis. Although the reaction of unsubstituted amidines or monosubstituted amidines having a normal alkyl group on the nitrogen atom and *α,β*-unsaturated carbonyl compounds gives pyrimidine derivatives [2-5], *N-t*-butylacetamidines **1** gave 2,3-dihydropyridine derivatives **4**. Obviously the bulkiness of the *N-t*-butyl group in the *N*-alkylated products **3** acts to suppress formation of a pyrimidine ring, resulting in derivatives **4** (Scheme 1). The suppression of cyclization by the *t*-butyl group was also confirmed by the following experiment. Heating *N-t*-butylbenzamidine and methyl vinyl ketone (**2** (R^2=H, R^3=Me)) at 120° for 3 hours produced only the *N*-alkylated product **11** (87 %); a cyclization product could not be isolated. In another reaction, a diglyme solution of **1a** and methyl vinyl ketone (**2** (R^2=H, R^3=Me)) was heated in a 120° oil bath for 2 hours, and **4a** was directly obtained in 67 % yield. Similarly, various *N-t*-butylacetamidines **1** were reacted with methyl vinyl ketone (**2** (R^2=H, R^3=Me)), acrolein (**2** (R^2=H, R^3= H)) or crotonaldehyde (**2** (R^2= Me, R^3= H)). The results for the obtained 2,3-dihydropyridine derivatives **4**, **5** and **6** are shown in Table 1.

Scheme 1



Reaction of *N-t*-butylacetamidines **1** with phenyl 1-propenyl ketone, benzalacetone or chalcone, in which the carbonyl groups is less electrophilic than that of methyl vinyl ketone, acrolein and crotonaldehyde [6], gave products resulting from *C*-alkylation of the amidines, as has been previously reported for *α,β*-unsaturated esters [1]. That is, a diglyme solution of *N-t*-butylbenzylamidine (**1a**) and phenyl 1-propenyl ketone (**2** (R^2=Me, R^3=Ph)) was heated in a 150° oil bath for 3 hours. The solvent was removed and deposited crystals were collected to obtain the 3,4-dihydropyridine derivative **8a** (60 %). The formation of **8a** is considered to proceed as follows (Scheme 1). Although this reaction tends toward *N*-alkylation, cyclization of the *N*-alkylated product **3a** (R^2=Me, R^3=Ph) does not take place because the carbonyl group in the *N*-alkylated product has low electrophilicity.

Table 1

Preparation of Compounds **4**, **5** and **6**

Compd.	R^1	R^2	R^3	Reaction Temp [°C]	Reaction Time [h]	Yield [%]
4a	Ph	H	Me	120	2	67
4b	4-Me-C_6H_4	H	Me	120	2	70
4c	4-MeO-C_6H_4	H	Me	120	2	70
4d	4-Cl-C_6H_4	H	Me	120	2	68
4e	4-Br-C_6H_4	H	Me	120	2	41
5a	Ph	H	H	150	1	79
5b	4-Me-C_6H	H	H	150	1	69
5c	4-MeO-C_6H_4	H	H	150	1	51
5d	4-Cl-C_6H_4	H	H	150	1	60
5e	4-Br-C_6H_4	H	H	150	2	43
6a	Ph	Me	H	120	2	81
6b	4-Me-C_6H_4	Me	H	120	3	69
6c	4-MeO-C_6H_4	Me	H	120	2	67
6d	4-Cl-C_6H_4	Me	H	120	4	67
6e	4-Br-C_6H_4	Me	H	120	4	57

As a result, **3a** (R^2=Me, R^3=Ph) undergoes the reverse reaction. A small amount of the *N,C*-tautomer of the amidine **1a**, that is, ene-1,1-diamine **1'a** [1], then reacts with **2** (R^2=Me, R^3=Ph) by Michael addition to produce a *C*-alkylated product **7a** (R^2=Me, R^3=Ph). Subsequently, the carbonyl group of **7a** (R^2=Me, R^3=Ph) undergoes strong nucleophilic attack from the imino nitrogen atom, and **8a** is formed through cyclodehydration. The structure of **8a** was confirmed by elemental analysis and spectroscopic measurements. Similarly, various *N-t*-butylacetamidines **1** were reacted with phenyl 1-propenyl ketone (**2** (R^2=Me, R^3=Ph)), benzalacetone (**2** (R^2= Ph, R^3= Me)) or chalcone (**2** (R^2= Ph, R^3=Ph)). The results of the obtained 3,4-dihydropyridine derivatives **8**, **9** and **10** are shown in Table 2.

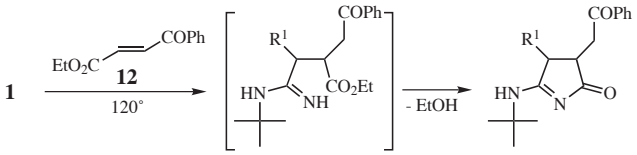
When a diglyme solution of the amidines **1** and ethyl 3-benzoylacrylate (**12**) was heated at 120°, 3,4-dihydropyrrol-2-one derivatives **13** were obtained (Scheme 2, Table 3). The structure of **13** was confirmed by elemental analysis, spectroscopic measurements and X-ray crystal structural analysis. The compounds **13** were formed by Michael addition of the amidines **1** as their *N,C*-tautomer ene-1,1-diamines **1'** to *α,β*-unsaturated ketone **12** and subsequent cyclization with elimination of ethyl alcohol.

Table 2

Preparation of Compounds **8**, **9** and **10**

Compd.	R^1	R^2	R^3	Reaction Temp [°C]	Reaction Time [h]	Yield [%]
8a	Ph	Me	Ph	150	3	60
8b	4-Me-C_6H_4	Me	Ph	150	3	58
8c	4-MeO-C_6H_4	Me	Ph	150	3	49
8d	4-Cl-C_6H_4	Me	Ph	150	3	61
8e	4-Br-C_6H_4	Me	Ph	150	3	55
9a	Ph	Ph	Me	150	4	67
9b	4-Me-C_6H_4	Ph	Me	150	4	43
9c	4-MeO-C_6H_4	Ph	Me	150	4	34
9d	4-Cl-C_6H_4	Ph	Me	150	3	54
9e	4-Br-C_6H_4	Ph	Me	150	3	49
10a	Ph	Ph	Ph	150	3	72
10b	4-Me-C_6H_4	Ph	Ph	150	4	62
10c	4-MeO-C_6H_4	Ph	Ph	150	3	78
10d	4-Cl-C_6H_4	Ph	Ph	150	3	91
10e	4-Br-C_6H_4	Ph	Ph	150	3	71

Scheme 2



13

Acetamidines **1** having a *t*-butyl group on the nitrogen atom were reacted with methyl vinyl ketone (**2** (R^2=H, R^3=Me)), acrolein (**2** (R^2=H, R^3= H)) or crotonaldehyde (**2** (R^2= Me, R^3= H)). The amidines **1** reacted as their *N,N'*-tautomer azaenamines, forming *N*-alkylated products **3**. Subsequent cyclodehydration of the *N*-alkylated products **3** gave the 2,3-dihydropyridine derivatives **4**, **5** and **6**. In contrast, in reaction with phenyl 1-propenyl ketone (**2** (R^2=Me, R^3=Ph)), benzalacetone (**2** (R^2= Ph, R^3= Me)) or chalcone (**2** (R^2= Ph, R^3=Ph)), the same acetamidines **1** reacted as their *N,C*-tautomer ene-1,1-diamines **1'**. Thus, the amidines **1** were *C*-alkylated by Michael addition to the *α,β*-unsaturated carbonyl compounds. Subsequent cyclodehydration of the Michael adducts **7** gave 3,4-dihydropyridine derivatives **8**, **9** and **10**. In addition, 3,4-dihydropyrrol-2-one derivatives **13** were obtained by reaction of the acetamidines **1** with ethyl 3-benzoylacrylate **12**.

Table 3

Preparation of Compounds **13**

Compd.	R^1	Reaction Temp[°C]	Reaction Time[h]	Yield[%]
13a	Ph	120	1	85
13b	4-Me-C_6H_4	120	2	78
13c	4-MeO-C_6H_4	120	2	77
13d	4-Cl-C_6H_4	120	2	77
13e	4-Br-C_6H_4	120	2	49

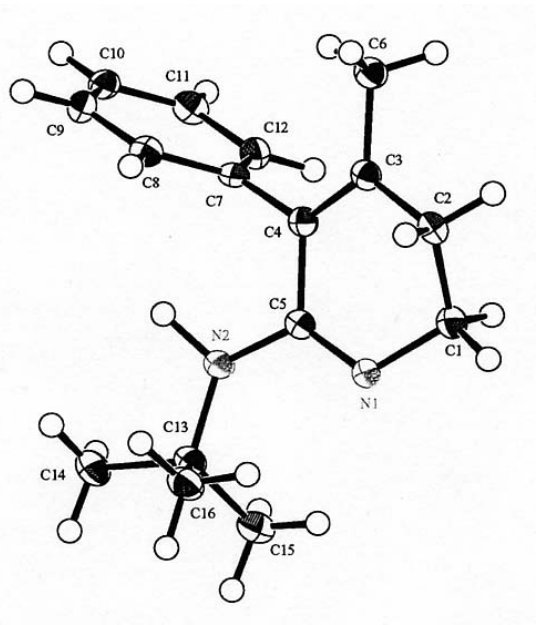


Figure 1 Crystal structure of compound **4a**.

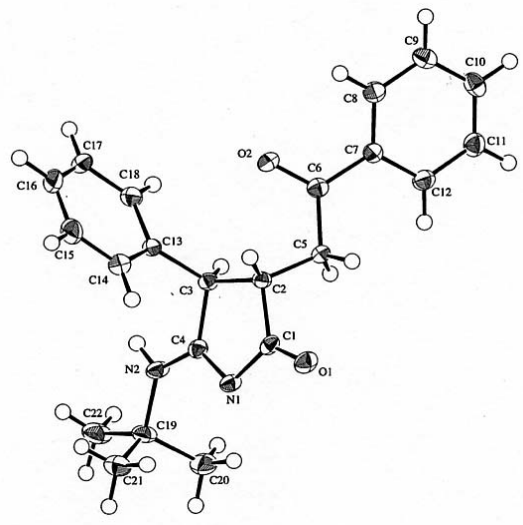


Figure 2 Crystal structure of compound **13a**

EXPERIMENTAL

All melting points and boiling points are uncorrected. The ir spectra were recorded on a Horiba FT-720 spectrometer in potassium bromide pellets unless otherwise noted. The ^{1}H nmr data were obtained with a JEOL JNM-EX400 (400 MHz) or a JEOL JNM-ECX500M (500 MHz) spectrometer in deuteriochloroform by using tetramethylsilane as an internal standard.

Mass spectra were measured with a Shimadzu GCMS-QP5050A spectrometer at 70 eV of ionization energy by use of a direct-inlet system. Elemental analyses were performed by using a Perkin-Elmer 2400 II CHN Analyzer. X-ray structure determinations were performed on Rigaku RAXIS-RAPID diffractometer, at the X-ray Research Laboratory, Rigaku Corporation.

N-t-Butylacetamidines **1** and *N-t*-Butylbenzamidine were prepared by the method of Cooper and Partridge [7]. Methyl vinyl ketone, acrolein, crotonaldehyde, pheyl 1-propenyl ketone, benzalacetone, chalcone and ethyl benzoylacrylate were commercially available and used without further purification.

N-t-Butyl-*N*'-(3-oxobutyl)-2-phenylacetamidine (**3a** (R^2=H, R^3=Me)).

A solution containing *N-t*-butylbenzylamidine (**1a**) (9.51 g, 50.0 mmoles) and methyl vinyl ketone (**2** (R^2=H, R^3=Me)) (4.21 g, 60.0 mmoles) in monoglyme (50 ml) was heated 50° for 3 hours. The solvent and the low boiling materials were removed under reduced pressure (at 0.12 mmHg), maintaining the bath temperature below 50°, leaving 12.32 g (95 %) of *N*-alkylation product **3a** (R^2=H, R^3=Me) as a pale yellow liquid. This product obtained was of satisfactory purity as judged by ^{1}H nmr spectroscopy, which was used without further purification; ir (liquid film): 3406, 1709, 1645, 1500, 1450 cm^{-1}; ^{1}H nmr: δ 1.28 (9H, s, $C(CH_3)_3$), 2.15 (3H, s, CH_3), 2.58 and 3.45 (each 2H, t, J=6.6 Hz, CH_2), 3.47 (2H, s, CH_2), 3.70 (1H, br s, NH), 7.16-7.31 (5H, m, aromatic); ms: (CI) m/z 261 (MH^+).

Anal. Calcd. for $C_{16}H_{24}N_2O$: C, 73.81; H, 9.29; N, 10.76. Found: C, 73.74; H, 9.51; N, 11.13.

Conversion to 2,3-Dihydropyridine Derivative **4a** of *N*-Alkylation Product **3a** (R^2=H, R^3=Me).

A solution of *N*-alkylation product **3a** (R^2=H, R^3=Me) (7.82 g, 30.0 mmoles) in diglyme (60 ml) was heated with stirring at 120° for 2 hours. Removal of the solvent under reduced pressure and distillation of the residue gave 1.71 g (30 %) of the acetamidine **1a** and 4.41 g (57 %) of the 2,3-dihydropyridine derivatives **4a**, and both have solidified by the standing.

N-t-Butyl-*N*'-(3-oxobutyl)-benzamidine (**11**).

A solution containing *N-t*-butylbenzamidine (3.53 g, 20.0 mmoles) and methyl vinyl ketone (**2** (R^2=H, R^3=Me)) (1.68 g, 24.0 mmoles) in diglyme (40 ml) was heated with stirring at 120° for 3 hours. After removal of the solvent under reduced pressure, the residual solid was recrystallized from ethyl acetate to give 4.29 g (87 %) of **11** as colorless prisms, mp 74.5-75.0°; ir: 3379, 1705, 1631, 1599, 1522, 1442 cm^{-1}; ^{1}H nmr: δ 1.38 (9H, s, $C(CH_3)_3$), 2.15 (3H, s, CH_3), 2.52 and 3.29 (each 2H, t, J=6.6 Hz, CH_2), 3.79 (1H, br s, NH), 7.21-7.37 (5H, m, aromatic); ms: (CI) m/z 247 (MH^+).

Anal. Calcd. for $C_{15}H_{22}N_2O$: C, 73.13; H, 9.00; N, 11.37. Found: C, 73.06; H, 9.24; N, 11.35.

2,3-Dihydropyridines **4**, **5** and **6**.

A solution containing *N-t*-butylacetamidines **1** (30.0 mmoles) and methyl vinyl ketone (**2** (R^2=H, R^3=Me)), acrolein (**2** (R^2=H, R^3=H)) or crotonaldehyde (2 (R^2=Me, R^3=H)) (36.0 mmoles) in diglyme (60 ml) was heated with stirring at the temperature indicated in Table 1. After removal of the solvent under reduced pressure, the resulting residue was distilled to give the products **4**, **5** or **6**. The products (except **5b**) has solidified by the standing. All the products obtaind were of satisfactory purity as judged by ^{1}H nmr spectroscopy. Analytical samples were prepared by recrystallization from ethyl acetate.

6-*t*-Butylamino-4-methyl-5-phenyl-2,3-dihydropyridine (**4a**).

This compound was obtained as pale yellow needles, mp 94.0-94.5°; bp 108.0-110.0° (0.35 mmHg); ir: 3429, 1658, 1597, 1512, 1448 cm^{-1}; ^{1}H nmr: δ 1.24 (9H, s, $C(CH_3)_3$), 1.68 (3H, s, CH_3), 2.12 and 3.48 (each 2H, t, J=7.6 Hz, CH_2), 3.50 (1H, br s, NH), 7.11-7.38 (5H, m, aromatic); ms: (CI) m/z 243 (MH^+).

Anal. Calcd. for $C_{16}H_{22}N_2$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.36; H, 9.28; N, 11.72.

X-Ray structure determinetion of compound **4a**.

Crystal of **4a** suitable for the structure analysis were obtained by recrystallization from ethyl acetate. The measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Cu-Kα (λ=1.54182 Å) radiation. The crystal structure was solved by direct methods (SIR97) and expanded using Fourier techniques (DIRDIF99) (Figure 1).

Crystal data: Empirical formula $C_{16}H_{22}N_2$; Formula weight 242.36; Crystal dimensions 0.20x0.12x0.07 mm; Crystal system orthorhombic; Lattice parameters a=6.588(5) Å, b=7.3586(6) Å, c=30.270(2) Å, V=1438.64(20) Å^3; Space group $P2_12_12_1$ (#19); Z value 4; D_{calc}=1.119 g/cm^3; F_{000}=528.00; μ(CuKα)=5.004 cm^{-1}; No. of reflections 2574; Residuals: R1 (1>2.00σ(I))=0.0343, R=0.0406, wR2=0.0860; Goodness of fit indicator 1.080.

6-*t*-Butylamino-4-methyl-5-(4-methylphenyl)-2,3-dihydropyridine (**4b**).

This compound was obtained as colorless prisms, mp 92.5-93.0°; bp 122.0-124.0° (0.55 mmHg); ir: 3427, 1662, 1603, 1510, 1446 cm^{-1}; ^{1}H nmr: δ 1.24 (9H, s, $C(CH_3)_3$), 1.67 (3H, s, CH_3), 2.10 and 3.46 (each 2H, t, J=7.6 Hz, CH_2), 2.37 (3H, s, CH_3), 3.56 (1H, br s, NH), 7.00 and 7.16 (each 2H, d, J=8.0 Hz, aromatic); ms: (CI) m/z 257 (MH^+).

Anal. Calcd. for $C_{17}H_{24}N_2$: C, 79.64; H, 9.43; N, 10.93. Found: C, 79.42; H, 9.75; N, 10.98.

6-*t*-Butylamino-4-methyl-5-(4-methoxyphenyl)-2,3-dihydropyridine (**4c**).

This compound was obtained as a pale orange powder, mp 76.0-77.0°; bp 140.0-144.0° (0.55 mmHg); ir: 3431, 1660, 1606, 1510, 1450 cm^{-1}; ^{1}H nmr: δ 1.24 (9H, s, $C(CH_3)_3$), 1.68 (3H, s, CH_3), 2.01 and 3.46 (each 2H, t, J=7.7 Hz, CH_2), 3.55 (1H, br s, NH), 3.83 (3H, s, CH_3O), 6.90 and 7.04 (each 2H, d, J=8.5 Hz, aromatic); ms: (CI) m/z 273 (MH^+).

Anal. Calcd. for $C_{17}H_{24}N_2O$: C, 74.96; H, 8.88; N, 10.28. Found: C, 74.75; H, 8.88; N, 10.10.

6-*t*-Butylamino-5-(4-chlorophenyl)-4-methyl-2,3-dihydropyridine (**4d**).

This compound was obtained as colorless prisms, mp 112.5-113.5°; bp 135.0-137.0° (1.10 mmHg); ir: 3429, 1660, 1604, 1510, 1489, 1448 cm^{-1}; ^{1}H nmr: δ 1.24 (9H, s, $C(CH_3)_3$), 1.67 (3H, s, CH_3), 2.11 and 3.46 (each 2H, t, J=7.6 Hz, CH_2), 3.38 (1H, br s, NH), 7.07 and 7.35 (each 2H, d, J=8.3 Hz, aromatic); ms: (CI) m/z 277 (MH^+).

Anal. Calcd. for $C_{16}H_{21}ClN_2$: C, 69.43; H, 7.65; N, 10.12. Found: C, 69.51; H, 7.84; N, 10.08.

5-(4-Bromophenyl)-6-*t*-butylamino-4-methyl-2,3-dihydropyridine (**4e**).

This compound was obtained as a white powder, mp 124.0-125.0°; ir: 3427, 1660, 1603, 1510, 1445, 1448 cm^{-1}; ^1H nmr: δ 1.25 (9H, s, $C(CH_3)_3$), 1.67 (3H, s, CH_3), 2.11 and 3.46 (each 2H, t, J=7.6 Hz, CH_2), 3.37 (1H, br s, NH), 7.01 and 7.50 (each 2H, d, J=8.3 Hz, aromatic); ms: (CI) m/z 321and 323 (MH^+).

Anal. Calcd. for $C_{16}H_{21}BrN_2$: C, 59.82; H, 6.59; N, 8.72. Found: C, 59.94; H, 6.62; N, 8.70.

6-*t*-Butylamino-5-phenyl-2,3-dihydropyridine (**5a**).

This compound was obtained as a white powder, mp 41.5-42.5°; bp 112.0-114.0° (0.40 mmHg); ir: 3433, 1647, 1591, 1508, 1450 cm^{-1}; ^1H nmr: δ 1.32 (9H, s, $C(CH_3)_3$), 2.15 (2H, td, J=7.6, 4.6 Hz, CH_2), 3.45 (2H, t, J=7.6 Hz, CH_2), 3.77 (1H, br s, NH), 6.37 (1H, t, J=4.6 Hz, CH), 7.26-7.36 (5H, m, aromatic); ms: (CI) m/z 229 (MH^+).

Anal. Calcd. for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27. Found: C, 78.68; H, 9.05; N, 12.17.

6-*t*-Butylamino-5-(4-methylphenyl)-2,3-dihydropyridine (**5b**).

This compound was obtained as a colorless liquid, bp 117.0-119.0° (0.70 mmHg); ir: (liquid film) 3437, 1649, 1589, 1510, 1450 cm^{-1}; ^1H nmr: δ 1.32 (9H, s, $C(CH_3)_3$), 2.13 (2H, td, J=7.6, 4.6 Hz, CH_2), 2.36 (3H, s, CH_3), 3.44 (2H, t, J=7.6 Hz, CH_2), 3.82 (1H, br s, NH), 6.34 (1H, t, J=4.6 Hz, CH), 7.15 (5H, s, aromatic); ms: (CI) m/z 243 (MH^+).

Anal. Calcd. for $C_{16}H_{22}N_2$: C, 79.29; H, 9.15; N, 11.56. Found: C, 78.95; H, 9.19; N, 11.28.

6-*t*-Butylamino-5-(4-methoxyphenyl)-2,3-dihydropyridine (**5c**).

This compound was obtained as pale orange prisms, mp 76.5-77.5°; bp 146-148.0° (1.10 mmHg); ir: 3442, 1649, 1608, 1591, 1508, 1466 cm^{-1}; ^1H nmr: δ 1.33 (9H, s, $C(CH_3)_3$), 2.13 (2H, td, J=7.6, 4.6 Hz, CH_2), 3.44 (2H, t, J=7.6 Hz, CH_2), 3.81 (1H, br s, NH), 3.83 (3H, s, CH_3O), 6.32 (1H, t, J=4.6 Hz, CH), 6.89 and 7.19 (each 2H, d, J=8.5 Hz, aromatic); ms: (CI) m/z 259 (MH^+).

Anal. Calcd. for $C_{16}H_{22}N_2O$: C, 74.38; H, 8.58; N, 10.84. Found: C, 74.03; H, 8.90; N, 10.75.

6-*t*-Butylamino-5-(4-chlorophenyl)-2,3-dihydropyridine (**5d**).

This compound was obtained as colorless prisms, mp 67.5-68.5°; bp 145.0-148.0° (1.70 mmHg); ir: 3438, 1651, 1597, 1508, 1483, 1448 cm^{-1}; ^1H nmr: δ 1.32 (9H, s, $C(CH_3)_3$), 2.14 (2H, td, J=7.6, 4.6 Hz, CH_2), 3.44 (2H, t, J=7.6 Hz, CH_2), 3.64 (1H, br s, NH), 6.36 (1H, t, J=4.6 Hz, CH), 7.20 and 7.32 (each 2H, d, J=8.4 Hz, aromatic); ms: (CI) m/z 263 (MH^+).

Anal. Calcd. for $C_{15}H_{19}ClN_2$: C, 68.56; H, 7.29; N, 10.66. Found: C, 68.79; H, 7.55; N, 10.79.

5-(4-Bromophenyl)-6-*t*-butylamino-2,3-dihydropyridine (**5e**).

This compound was obtained as a white powder, mp 79.0-80.0°; ir: 3433, 1655, 1637, 1597, 1572, 1514, 1481, 1446 cm^{-1}; ^1H nmr: δ 1.32 (9H, s, $C(CH_3)_3$), 2.14 (2H, td, J=7.6, 4.6 Hz, CH_2), 3.44 (2H, t, J=7.6 Hz, CH_2), 3.64 (1H, br s, NH), 6.37 (1H, t, J=4.6 Hz, CH), 7.14 and 7.48 (each 2H, d, J=8.3 Hz, aromatic); ms: (CI) m/z 307 and 309 (MH^+).

Anal. Calcd. for $C_{15}H_{19}BrN_2$: C, 58.64; H, 6.23; N, 9.12. Found: C, 58.83; H, 6.28; N, 9.24.

6-*t*-Butylamino-2-methyl-5-phenyl-2,3-dihydropyridine (**6a**).

This compound was obtained as colorless prisms, mp 43.5-44.5°; bp 107.0-110.0° (1.00 mmHg); ir: 3438, 1649, 1591, 1506, 1448 cm^{-1}; ^1H nmr: δ 1.25 (3H, d, J=6.8 Hz, CH_3), 1.33 (9H, s, $C(CH_3)_3$), 1.87 (1H, ddd, J=16.8, 11.6, 3.7 Hz, CH_2), 2.23 (1H, ddd, J=16.8, 5.6, 5.6 Hz, CH_2), 3.50 (1H, m, CH_3CH) 3.66 (1H, br s, NH), 6.24 (1H, dd, J=5.6, 3.7 Hz, CH), 7.23-7.34 (5H, m, aromatic); ms: (CI) m/z 243 (MH^+).

Anal. Calcd. for $C_{16}H_{22}N_2$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.25; H, 9.39; N, 11.58.

6-*t*-Butylamino-2-methyl-5-(4-methylphenyl)-2,3-dihydropyridine (**6b**).

This compound was obtained as pale yellow prisms, mp 54.0-55.0°; bp 115.0-117.0° (0.45 mmHg); ir: 3437, 1651, 1593, 1506, 1448 cm^{-1}; ^1H nmr: δ 1.24 (3H, d, J=6.7 Hz, CH_3), 1.33 (9H, s, $C(CH_3)_3$), 1.86 (1H, ddd, J=16.8, 11.5, 3.7 Hz, CH_2), 2.23 (1H, ddd, J=16.8, 5.6, 5.6 Hz, CH_2), 2.35 (3H, s, CH_3), 3.49 (1H, m, CH_3CH) 3.70 (1H, br s, NH), 6.22 (1H, dd, J=5.6, 3.7 Hz, CH), 7.14 (4H, s, aromatic); ms: (CI) m/z 257 (MH^+).

Anal. Calcd. for $C_{17}H_{24}N_2$: C, 79.64; H, 9.43; N, 10.93. Found: C, 79.79; H, 9.53; N, 10.68.

6-*t*-Butylamino-5-(4-methoxyphenyl)-2-methyl-2,3-dihydropyridine (**6c**).

This compound was obtained as orange prisms, mp 65.0-66.5°; bp 138.0-140.0° (1.10 mmHg); ir: 3406, 1645, 1608, 1583, 1508, 1442 cm^{-1}; ^1H nmr: δ 1.24 (3H, d, J=6.6 Hz, CH_3), 1.33 (9H, s, $C(CH_3)_3$), 1.86 (1H, ddd, J=16.8, 11.7, 3.7 Hz, CH_2), 2.23 (1H, ddd, J=16.8, 5.6, 5.6 Hz, CH_2), 3.49 (1H, m, CH_3CH) 3.70 (1H, br s, NH), 3.82 (3H, s, CH_3O), 6.19 (1H, dd, J=5.6, 3.7 Hz, CH), 6.88 and 7.18 (each 2H, d, J=8.8 Hz, aromatic); ms: (CI) m/z 273 (MH^+).

Anal. Calcd. for $C_{17}H_{24}N_2O$: C, 74.96; H, 8.88; N, 10.28. Found: C, 74.93; H, 9.04; N, 10.34.

6-*t*-Butylamino-5-(4-chlorophenyl)-2-methyl-2,3-dihydropyridine (**6d**).

This compound was obtained as colorless prisms, mp 66.0-67.0°; bp 125.0-127.0° (0.40 mmHg); ir: 3442, 1647, 1587, 1508, 1489, 1448 cm^{-1}; ^1H nmr: δ 1.24 (3H, d, J=6.9 Hz, CH_3), 1.33 (9H, s, $C(CH_3)_3$), 1.87 (1H, ddd, J=16.6, 11.5, 3.4 Hz, CH_2), 2.24 (1H, ddd, J=16.6, 5.7, 5.7 Hz, CH_2), 3.49 (1H, m, CH_3CH) 3.55 (1H, br s, NH), 6.25 (1H, dd, J=5.7, 3.4 Hz, CH), 7.20 and 7.31 (each 2H, d, J=8.6 Hz, aromatic); ms: (CI) m/z 277 (MH^+).

Anal. Calcd. for $C_{16}H_{21}ClN_2$: C, 69.43; H, 7.65; N, 10.12. Found: C, 69.69; H, 7.76; N, 10.24.

5-(4-Bromophenyl)-6-*t*-butylamino-2-methyl-2,3-dihydropyridine (**6e**).

This compound was obtained as colorless prisms, mp 82.0-83.0°; bp 137.0-139.0° (0.45 mmHg); ir: 3440, 1645, 1587, 1510, 1485, 1450 cm^{-1}; ^1H nmr: δ 1.24 (3H, d, J=6.9 Hz, CH_3), 1.33 (9H, s, $C(CH_3)_3$), 1.86 (1H, ddd, J=16.6, 11.5, 3.4 Hz, CH_2), 2.24 (1H, ddd, J=16.6, 5.7, 5.7 Hz, CH_2), 3.48 (1H, m, CH_3CH) 3.55 (1H, br s, NH), 6.26 (1H, dd, J=5.7, 3.4 Hz, CH), 7.14 and 7.47 (each 2H, d, J=8.6 Hz, aromatic); ms: (CI) m/z 321 and 323 (MH^+).

Anal. Calcd. for $C_{16}H_{21}BrN_2$: C, 59.82; H, 6.59; N, 8.72. Found: C, 59.90; H, 6.54; N, 8.80.

3,4-Dihydropyridines **8**.

A solution containing *N*-*t*-butylacetamidines **1** (20.0 mmoles) and phenyl 1-propenyl ketone (**2** (R^2=Me, R^3=Ph)) (24.0 mmoles) in diglyme (40 ml) was heated with stirring at 150° for 3 hours. After removal of the solvent under reduced pressure, deposited crystals were collected and washed with small amount of ethyl acetate to give **8**. All the products obtained were of satisfactory purity as judged by ^{1}H nmr spectroscopy. Analytical samples were prepared by further recrystallization from ethyl acetate.

2-*t*-Butylamino-4-methyl-3,6-diphenyl-3,4-dihydropyridine (**8a**).

This compound was obtained as colorless prisms, mp 106.5-107.5°; ir: 3425, 1610, 1587, 1520, 1493, 1542 cm^{-1}; ^{1}H nmr: δ 1.00 (3H, d, J=6.9 Hz, CH_3), 1.42 (9H, s, $C(CH_3)_3$), 2.64 (1H, dqd, J=9.7, 6.9, 4.0 Hz, CH), 2.97 (1H, d, J=9.8 Hz, CH), 4.01 (1H, br s, NH), 5.61 (1H, d, J=4.0 Hz, CH), 7.17-7.36 and 7.84-7.87 (10H, m, aromatic); ms: (CI) m/z 319 (MH^+).

Anal. Calcd. for $C_{22}H_{26}N_2$: C, 82.97; H, 8.23; N, 8.80. Found: C, 82.87; H, 8.24; N, 8.72.

2-*t*-Butylamino-4-methyl-3-(4-methylphenyl)-6-phenyl-3,4-dihydropyridine (**8b**).

This compound was obtained as colorless prisms, mp 138.5-140.0°; ir: 3423, 1637, 1593, 1513, 1491, 1446 cm^{-1}; ^{1}H nmr: δ 0.99 (3H, d, J=6.9 Hz, CH_3), 1.42 (9H, s, $C(CH_3)_3$), 2.33 (3H, s, CH_3), 2.61 (1H, dqd, J=10.3, 6.9, 4.0 Hz, CH), 2.93 (1H, d, J=10.3 Hz, CH), 4.05 (1H, br s, NH), 5.60 (1H, d, J=4.0 Hz, CH), 7.06-7.35 and 7.85-7.87 (9H, m, aromatic); ms: (CI) m/z 333 (MH^+).

Anal. Calcd. for $C_{23}H_{28}N_2$: C, 83.09; H, 8.49; N, 8.48. Found: C, 83.48; H, 8.50; N, 8.60.

2-*t*-Butylamino-3-(4-methoxyphenyl)-4-methyl-6-phenyl-3,4-dihydropyridine (**8c**).

This compound was obtained as pale yellow prisms, mp 144.5-145.5°; ir: 3417, 1608, 1585, 1510, 1492, 1448 cm^{-1}; ^{1}H nmr: δ 0.98 (3H, d, J=6.9 Hz, CH_3), 1.42 (9H, s, $C(CH_3)_3$), 2.60 (1H, dqd, J=10.3, 6.9, 4.0 Hz, CH), 2.93 (1H, d, J=10.3 Hz, CH), 3.78 (3H, s, CH_3O), 4.06 (1H, br s, NH), 5.61 (1H, d, J=4.0 Hz, CH), 6.84-7.35 and 7.85-7.87 (9H, m, aromatic); ms: (CI) m/z 349 (MH^+).

Anal. Calcd. for $C_{23}H_{28}N_2O$: C, 79.27; H, 8.10; N, 8.04. Found: C, 79.58; H, 8.20; N, 8.20.

2-*t*-Butylamino-3-(4-chlorophenyl)-4-methyl-6-phenyl-3,4-dihydropyridine (**8d**).

This compound was obtained as colorless prisms, mp 158.0-159.5°; ir: 3425, 1655, 1591, 1513, 1485, 1446 cm^{-1}; ^{1}H nmr: δ 1.01 (3H, d, J=6.9 Hz, CH_3), 1.44 (9H, s, $C(CH_3)_3$), 2.55 (1H, dqd, J=8.6, 6.9, 4.6 Hz, CH), 2.94 (1H, d, J=8.6 Hz, CH), 3.99 (1H, br s, NH), 5.58 (1H, d, J=4.6 Hz, CH), 7.09-7.36 and 7.83-7.85 (9H, m, aromatic); ms: (CI) m/z 353 (MH^+).

Anal. Calcd. for $C_{22}H_{25}ClN_2$: C, 74.88; H, 7.14; N, 7.94. Found: C, 74.56; H, 7.03; N, 8.05.

3-(4-Bromophenyl)-2-*t*-butylamino-4-methyl-6-phenyl-3,4-dihydropyridine (**8e**).

This compound was obtained as colorless prisms, mp 162.0-163.5°; ir: 3425, 1655, 1593, 1512, 1481, 1446 cm^{-1}; ^{1}H nmr: δ 1.02 (3H, d, J=6.9 Hz, CH_3), 1.44 (9H, s, $C(CH_3)_3$), 2.54 (1H, dqd, J=8.6, 6.9, 4.6 Hz, CH), 2.92 (1H, d, J=8.6 Hz, CH), 3.99 (1H, br s, NH), 5.58 (1H, d, J=4.6 Hz, CH), 7.04-7.44 and 7.83-7.85 (9H, m, aromatic); ms: (CI) m/z 397 and 399 (MH^+).

Anal. Calcd. for $C_{22}H_{25}BrN_2$: C, 66.50; H, 6.34; N, 7.05. Found: C, 66.14; H, 6.05; N, 7.09.

3,4-Dihydropyridines **9**.

A solution containing *N*-*t*-butylacetamidines **1** (30.0 mmoles) and benzalacetone (**2** (R^2=Ph, R^3=Me)) (33.0 mmoles) in diglyme (60 ml) was heated with stirring at 150° for the time indicated in Table 2. After removal of the solvent under reduced pressure, the resulting residue was distilled to give **9**. The product **9c**, **9d** and **9e** had solidified by the standing. All the products obtained were of satisfactory purity as judged by ^{1}H nmr spectroscopy. Samples for analysis were recrystallized from ethyl acetate.

2-*t*-Butylamino-6-methyl-3,4-diphenyl-3,4-dihydropyridine (**9a**).

This compound was obtained as pale yellow liquid, bp 150.0-153.0° (0.40 mmHg); ir (liquid film): 3429, 1637, 1595, 1516, 1452 cm^{-1}; ^{1}H nmr: δ 1.35 (9H, s, $C(CH_3)_3$), 1.98 (3H, d, J=1.2 Hz, CH_3), 3.21 (1H, d, J=6.1 Hz, CH), 3.41 (1H, dd, J=6.1, 4.9 Hz, CH), 3.89 (1H, br s, NH), 4.86 (1H, dq, J=4.9, 1.2 Hz, CH), 7.14-7.29 (10H, m, aromatic); ms: (CI) m/z 319 (MH^+).

Anal. Calcd. for $C_{22}H_{26}N_2$: C, 82.97; H, 8.23; N, 8.80. Found: C, 83.34; H, 8.22; N, 8.97.

2-*t*-Butylamino-6-methyl-3-(4-methylphenyl)-4-phenyl-3,4-dihydropyridine (**9b**).

This compound was obtained as pale yellow liquid, bp 172.0-175.0° (0.70 mmHg); ir (liquid film): 3425, 1639, 1595, 1514, 1450 cm^{-1}; ^{1}H nmr: δ 1.34 (9H, s, $C(CH_3)_3$), 1.98 (3H, d, J=1.1 Hz, CH_3), 2.30 (3H, s, CH_3), 3.18 (1H, d, J=6.3 Hz, CH), 3.38 (1H, dd, J=6.3, 5.2 Hz, CH), 3.92 (1H, br s, NH), 4.85 (1H, dq, J=5.2, 1.1 Hz, CH), 7.03-7.22 (9H, m, aromatic); ms: (CI) m/z 333 (MH^+).

Anal. Calcd. for $C_{23}H_{28}N_2$: C, 83.09; H, 8.49; N, 8.43. Found: C, 83.07; H, 8.49; N, 8.42.

2-*t*-Butylamino-3-(4-methoxyphenyl)-6-methyl-4-phenyl-3,4-dihydropyridine (**9c**).

This compound was obtained as colorless prisms, mp 143.5-144.5°; bp 180.0-183.0° (0.30 mmHg); ir: 3415, 1637, 1589, 1529, 1508, 1452 cm^{-1}; ^{1}H nmr: δ 1.35 (9H, s, $C(CH_3)_3$), 1.99 (3H, dd, J=1.4, 1.3 Hz, CH_3), 3.18 (1H, d, J=6.8 Hz, CH), 3.39 (1H, ddq, J=6.8, 4.7, 1.4 Hz, CH), 3.78 (3H, s, CH_3O), 3.94 (1H, br s, NH), 4.88 (1H, dq, J=4.7, 1.3 Hz, CH), 6.81 and 7.05 (each 2H, d, J=8.6 Hz, aromatic), 7.13-7.25 (5H, m, aromatic); ms: (CI) m/z 349 (MH^+).

Anal. Calcd. for $C_{23}H_{28}N_2O$: C, 79.27; H, 8.10; N, 8.04. Found: C, 79.17; H, 8.16; N, 7.94.

2-*t*-Butylamino-3-(4-chlorophenyl)-6-methyl-4-phenyl-3,4-dihydropyridine (**9d**).

This compound was obtained as colorless prisms, mp 96.0-97.5°; bp 176.0-179.0° (0.50 mmHg); ir: 3444, 1637, 1593, 1522, 1487, 1450 cm^{-1}; ^{1}H nmr: δ 1.36 (9H, s, $C(CH_3)_3$), 1.99

(3H, dd, J=1.4, 1.3 Hz, CH_3), 3.17 (1H, d, J=5.7 Hz, CH), 3.35 (1H, ddq, J=5.7, 5.0, 1.4 Hz, CH), 3.88 (1H, br s, NH), 4.87 (1H, dq, J=5.0, 1.3 Hz, CH), 7.08-7.26 (9H, m, aromatic); ms: (CI) m/z 353 (MH^+).

Anal. Calcd. for $C_{22}H_{25}ClN_2$: C, 74.88; H, 7.14; N, 7.94. Found: C, 75.01; H, 7.18; N, 7.83.

3-(4-Bromophenyl)-2-*t*-Butylamino-6-methyl-4-phenyl-3,4-dihydropyridine (**9e**).

This compound was obtained as colorless prisms, mp 113.0-114.5°; bp 187.0-190.0° (0.40 mmHg); ir: 3440, 1637, 1593, 1522, 1483, 1450 cm^{-1}; ^1H nmr: δ 1.36 (9H, s, $C(CH_3)_3$), 1.98 (3H, dd, J=1.4, 1.3 Hz, CH_3), 3.15 (1H, d, J=5.4 Hz, CH), 3.34 (1H, ddq, J=5.4, 5.0, 1.4 Hz, CH), 3.88 (1H, br s, NH), 4.86 (1H, dq, J=5.0, 1.3 Hz, CH), 7.03 and 7.40 (each 2H, d, J=8.6 Hz, aromatic), 7.14-7.26 (5H, m, aromatic); ms: (CI) m/z 397 and 399 (MH^+).

Anal. Calcd. for $C_{22}H_{25}BrN_2$: C, 66.50; H, 6.34; N, 7.05. Found: C, 66.24; H, 6.27; N, 6.99.

3,4-Dihydropyridines **10**.

A solution containing *N*-*t*-butylacetamidines **1** (20.0 mmoles) and chalcone (**2** (R^2=Ph, R^3=Ph)) (20.0 mmoles) in diglyme (40 ml) was heated with stirring at 150° for the time indicated in Table 2. After removal of the solvent under reduced pressure, the residue was recrystallized from ethyl acetate to give **10**. All the products obtained were of satisfactory purity as judged by ^1H nmr spectroscopy. Analytical samples were prepared by further recrystallization from ethyl acetate.

2-*t*-Butylamino-3,4,6-triphenyl-3,4-dihydropyridine (**10a**).

This compound was obtained as a white powder, mp 123.5-125.0°; ir: 3425、1587, 1510, 1491, 1450 cm^{-1}; ^1H nmr: δ 1.44 (9H, s, $C(CH_3)_3$), 3.34 (1H, d, J=5.8 Hz, CH), 3.65 (1H, dd, J=5.8, 5.4 Hz, CH), 4.10 (1H, br s, NH), 5.72 (1H, d, J=5.4 Hz, CH), 7.18-7.39 and 7.91-7.93 (15H, m, aromatic); ms: (CI) m/z 381 (MH^+).

Anal. Calcd. for $C_{27}H_{28}N_2$: C, 85.22; H, 7.42; N, 7.36. Found: C, 84.88; H, 7.59; N, 7.33.

2-*t*-Butylamino-3-(4-methylphenyl)-4,6-diphenyl-3,4-dihydropyridine (**10b**).

This compound was obtained as a white powder, mp 121.5-123.0°; ir: 3421, 1583, 1516, 1493, 1446 cm^{-1}; ^1H nmr: δ 1.44 (9H, s, $C(CH_3)_3$), 2.29 (3H, s, CH_3), 3.30 (1H, d, J=5.9 Hz, CH), 3.63 (1H, dd, J=5.9, 5.1 Hz, CH), 4.11 (1H, br s, NH), 5.71 (1H, d, J=5.1 Hz, CH), 7.02-7.38 and 7.91-7.93 (14H, m, aromatic); ms: (CI) m/z 395 (MH^+).

Anal. Calcd. for $C_{28}H_{30}N_2$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.52; H, 7.75; N, 7.13.

2-*t*-Butylamino-3-(4-methoxyphenyl)-4,6-diphenyl-3,4-dihydropyridine (**10c**).

This compound was obtained as a pale yellow powder, mp 140.5-141.0°; ir: 3421, 1610, 1587, 1512, 1491, 1444 cm^{-1}; ^1H nmr: δ 1.44 (9H, s, $C(CH_3)_3$), 3.30 (1H, d, J=6.3 Hz, CH), 3.62 (1H, dd, J=6.3, 5.1 Hz, CH), 3.76 (3H, s, CH_3O), 4.12 (1H, br s, NH), 5.73 (1H, d, J=5.1 Hz, CH), 6.80 and 7.10 (each 2H, d, J=8.8 Hz, aromatic), 7.18-7.39 and 7.91-7.93 (10H, m, aromatic); ms: (CI) m/z 411 (MH^+).

Anal. Calcd. for $C_{28}H_{30}N_2O$: C, 81.91; H, 7.36; N, 6.82. Found: C, 81.78; H, 7.56; N, 7.16.

2-*t*-Butylamino-3-(4-chlorophenyl)-4,6-diphenyl-3,4-dihydropyridine (**10d**).

This compound was obtained as white prisms, mp 151.5-152.0°; ir: 3429, 1581, 1518, 1491, 1446 cm^{-1}; ^1H nmr: δ 1.44 (9H, s, $C(CH_3)_3$), 3.29 (1H, d, J=4.6 Hz, CH), 3.58 (1H, dd, J=5.7, 4.6 Hz, CH), 4.06 (1H, br s, NH), 5.70 (1H, d, J=5.7 Hz, CH), 7.11-7.38 and 7.90-7.92 (14H, m, aromatic); ms: (CI) m/z 415 (MH^+).

Anal. Calcd. for $C_{27}H_{27}ClN_2$: C, 78.15; H, 6.56; N, 6.75. Found: C, 78.15; H, 6.51; N, 6.81.

3-(4-Bromophenyl)-2-*t*-butylamino-4,6-diphenyl-3,4-dihydropyridine (**10e**).

This compound was obtained as colorless prisms, mp 158.5-160.0°; ir: 3429, 1581, 1517, 1491, 1446 cm^{-1}; ^1H nmr: δ 1.44 (9H, s, $C(CH_3)_3$), 3.27 (1H, d, J=4.6 Hz, CH), 3.57 (1H, dd, J=5.7, 4.6 Hz, CH), 4.06 (1H, br s, NH), 5.70 (1H, d, J=5.7 Hz, CH), 7.05-7.39 and 7.89-7.91 (14H, m, aromatic); ms: (CI) m/z 459 and 461 (MH^+).

Anal. Calcd. for $C_{27}H_{27}BrN_2$: C, 70.59; H, 5.92; N, 6.10. Found: C, 70.93; H, 5.96; N, 6.18.

3,4-Dihydropyrrol-2-ones **13**.

A solution containing *N*-*t*-butylacetamidines **1** (20.0 mmoles) and ethyl 3-benzoylacrylate (**12**) (24.0 mmoles) in diglyme (40 ml) was heated with stirring at 120° for the time indicated in Table 3. The reaction mixture was cooled, and the precipitated product **13** was collected by filtration and washed with ethyl acetate. Evaporation of combined filtrates under reduced pressure and recrystallization of the residual solid from a small amount of ethyl acetate, gave an additional amount of product **13**. All the products obtained were of satisfactory purity as judged by ^1H nmr spectroscopy. Analytical samples were prepared by further recrystallization from ethyl acetate.

5-*t*-Butylamino-3-(2-oxopropyl)-4-phenyl-3,4-dihydropyrrol-2-one (**13a**).

This compound was obtained as a white powder, mp 232.5-233.0°; ir: 3296, 1712, 1678, 1572, 1545, 1450 cm^{-1}; ^1H nmr: δ 1.42 (9H, s, $C(CH_3)_3$), 3.02 (1H, ddd, J=8.6, 5.1, 3.4 Hz, CH), 3.29 (1H, dd, J=17.6, 8.6 Hz, CH_2), 3.68 (1H, dd, J=17.6, 3.4 Hz, CH_2), 3.91 (1H, d, J=5.1 Hz, CH), 5.03 (1H, br s, NH), 7.12-7.56 and 7.89-7.92 (10H, m, aromatic); ms: (CI) m/z 349 (MH^+).

Anal. Calcd. for $C_{22}H_{24}N_2O_2$: C, 75.83; H, 6.94; N, 8.04. Found: C, 75.77; H, 7.03; N, 8.07.

X-Ray structure determinetion of compound **13a**.

Crystal of **13a** suitable for the structure analysis were obtained by recrystallization from ethyl acetate. The measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα (λ=0.71069 Å) radiation. The crystal structure was solved by direct methods (SIR97) and expanded using Fourier techniques (DIRDIF94) (Figure 2).

Crystal data: Empirical formula $C_{22}H_{24}N_2O_2$; Formula weight 348.44; Crystal dimensions 0.20x0.10x0.10 mm; Crystal system monoclinic; Lattice parameters a=13.6524(4) Å, b=8.3703(3) Å,

c=16.3741(6) Å, β=97.8278(8)°, V=1853.7(1) Å^3; Space group $P2_1/n$ (#14); Z value 4; D_{calc}=1.248 g/cm^3; F_{000}=744.00; μ(MoKα)=0.80 cm^{-1}; No. of reflections 21960; Residuals: R1=0.043, R=0.074, wR=0.054; Goodness of fit indicator 1.11.

5-*t*-Butylamino-4-(4-methylphenyl)-3-(2-oxopropyl)-3,4-dihydropyrrol-2-one (**13b**).

This compound was obtained as a pale yellow powder, mp 212.0-213.0°; ir: 3332, 1720, 1680, 1562, 1543, 1514, 1450 cm^{-1}; ^{1}H nmr: δ 1.42 (9H, s, $C(CH_3)_3$), 2.34 (3H, s, CH_3), 3.00 (1H, ddd, J=8.6, 5.2, 3.4 Hz, CH), 3.28 (1H, dd, J=17.7, 8.6 Hz, CH_2), 3.65 (1H, dd, J=17.7, 3.4 Hz, CH_2), 3.87 (1H, d, J=5.2 Hz, CH), 5.03 (1H, br s, NH), 7.01 and 7.16 (each 2H, d, J=8.0 Hz, aromatic), 7.40-7.90 (5H, m, aromatic); ms: (CI) m/z 363 (MH^+).

Anal. Calcd. for $C_{23}H_{26}N_2O_2$: C, 76.21; H, 7.23; N, 7.73. Found: C, 75.94; H, 7.41; N, 7.75.

5-*t*-Butylamino-4-(4-methoxyphenyl)-3-(2-oxopropyl)-3,4-dihydropyrrol-2-one (**13c**).

This compound was obtained as a pale yellow powder, mp 201.5-203.0°; ir: 3334, 1720, 1678, 1562, 1541, 1512, 1448 cm^{-1}; ^{1}H nmr: δ 1.42 (9H, s, $C(CH_3)_3$), 2.98 (1H, ddd, J=8.7, 5.1, 3.5 Hz, CH), 3.26 (1H, dd, J=17.5, 8.7 Hz, CH_2), 3.67 (1H, dd, J=17.5, 3.5 Hz, CH_2), 3.81 (3H, s, CH_3O), 3.85 (1H, d, J=5.1 Hz, CH), 5.02 (1H, br s, NH), 6.88 and 7.04 (each 2H, d, J=8.7 Hz, aromatic), 7.40-7.91 (5H, m, aromatic); ms: (CI) m/z 379 (MH^+).

Anal. Calcd. for $C_{23}H_{26}N_2O_3$: C, 72.99; H, 6.92; N, 7.40. Found: C, 72.83; H, 6.91; N, 7.46.

5-*t*-Butylamino-4-(4-chlorophenyl)-3-(2-oxopropyl)-3,4-dihydropyrrol-2-one (**13d**).

This compound was obtained as a pale yellow powder, mp 151.5-153.0°; ir: 3327, 1722, 1672, 1562, 1547, 1491, 1450 cm^{-1}; ^{1}H nmr: δ 1.43 (9H, s, $C(CH_3)_3$), 2.96 (1H, ddd, J=9.3, 4.9, 3.2 Hz, CH), 3.24 (1H, dd, J=17.6, 9.3 Hz, CH_2), 3.71 (1H, dd, J=17.6, 3.2 Hz, CH_2), 3.86 (1H, d, J=4.9 Hz, CH), 5.03 (1H, br s, NH), 7.09 and 7.35 (each 2H, d, J=8.3 Hz, aromatic), 7.41-7.91 (5H, m, aromatic); ms: (CI) m/z 383 (MH^+).

Anal. Calcd. for $C_{22}H_{23}ClN_2O_2$: C, 69.01; H, 6.05; N, 7.32. Found: C, 69.26; H, 6.12; N, 7.31.

4-(4-Bromophenyl)-5-*t*-butylamino-3-(2-oxopropyl)-3,4-dihydropyrrol-2-one (**13e**).

This compound was obtained as a white powder, mp 185.0-187.0°; ir: 3232, 1701, 1689, 1585, 1535, 1479, 1448 cm^{-1}; ^{1}H nmr: δ 1.43 (9H, s, $C(CH_3)_3$), 2.96 (1H, ddd, J=9.2, 4.9, 3.3 Hz, CH), 3.24 (1H, dd, J=17.7, 9.2 Hz, CH_2), 3.70 (1H, dd, J=17.7, 3.3 Hz, CH_2), 3.85 (1H, d, J=4.9 Hz, CH), 5.04 (1H, br s, NH), 7.03 and 7.50 (each 2H, d, J=8.5 Hz, aromatic), 7.41-7.92 (5H, m, aromatic); ms: (CI) m/z 427 and 429 (MH^+).

Anal. Calcd. for $C_{22}H_{23}BrN_2O_2$: C, 61.83; H, 5.42; N, 6.56. Found: C, 61.88; H, 5.40; N, 6.53.

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