BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3556—3560 (1970)

The Syntheses of 2-Phenethyl-2,3-dihydro-4(1*H*)-pyridones

Noboru Sugiyama, Makoto Yamamoto and Choji Kashima

Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo

(Received June 15, 1970)

In the presence of three moles of potassium amide in liquid ammonia, the reactions of β-diketones with cinnamylidenaniline gave derivatives of 1-phenyl-2-styryl-2,3-dihydro-4-pyridone. By the catalytic hydrogenation of 6-methyl-1-phenyl-2-styryl-2,3-dihydro-4-pyridone, 6-methyl-2-phenethyl-1-phenyl-2,3-dihydro-4-pyridone was obtained. When β-diketones were treated with cinnamaldehyde azine, instead of cinnamylidenaniline, 1-cinnamylidenamino-2-styryl-2,3-dihydro-4-pyridones were produced; these were then catalytically hydrogenated to the corresponding 2-phenethyl-2,3-dihydro-4(1*H*)-pyridones, accompanied with 2-phenethyl-1-(3-phenylpropylamino)-2,3-dihydro-4-pyridones.

In the presence of three moles of potassium amide in liquid ammonia, dihydropyridone derivatives (A) which contain two phenyl groups at the 1- and 2-positions have been synthesized from β-diketones and benzylidenaniline.[1] The reactions of acetylacetone (**1**) with ethylidenaniline or benzylidenemethylamine, instead of benzylidenaniline, did not give the corresponding 1-phenyl- or 2-phenyl-dihydropyridone.[1]

The condensation of β-diketones with benzaldazine yielded 1-benzylidenamino-2,3-dihydro-4-pyridones,[2] which were then catalytically hydro-

---

[1] N. Sugiyama, M. Yamamoto and C. Kashima, This Bulletin, **42**, 1357 (1969).

[2] N. Sugiyama, M. Yamamoto and C. Kashima, *ibid.*, **43**, 901 (1970).

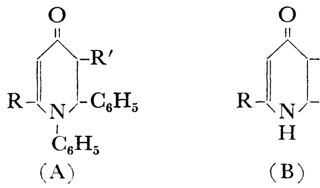

(A) (B)

Fig. 1.

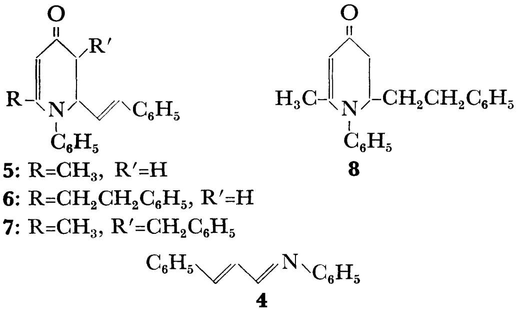
genolyzed to the corresponding 2,3-dihydro-4(1*H*)-pyridones (B). According to this procedure, dihydropyridone with a phenyl group at the 2-position was obtained.

The condensation of β-diketones with cinnamylidenaniline gave 2-styryl-dihydropyridones, which were then catalytically hydrogenated to the dihydropyridones with the phenethyl group at the 2-position.

Results and Discussion

In an attempt to synthesize dihydropyridones with aliphatic substituents, 1-phenyl-dihydropyridones with an aliphatic substituent at the C-2 position was synthesized first.

The reaction of acetylacetone (**1**) with cinnamylidenaniline (**4**) in the presence of sodium or potassium amide in liquid ammonia produced 6-methyl-1-phenyl-2-styryl-2,3-dihydro-4-pyridone (**5**). When three moles of sodium amide and one mole of **4** to **1** were used, the yield of **5** was 4.5%. When two moles of potassium amide were used, the yield of **5** was 5.8%. The mole ratio of 1 : 1 : 3 for **1**, **4** and potassium amide is the best condition for this reaction; this yield was 13.1%.


5: $R=CH_3$, $R'=H$

6: $R=CH_2CH_2C_6H_5$, $R'=H$

7: $R=CH_3$, $R'=CH_2C_6H_5$

8

4

Fig. 2.

The structure of **5** was determined by studying the spectral data and by elemental analyses.

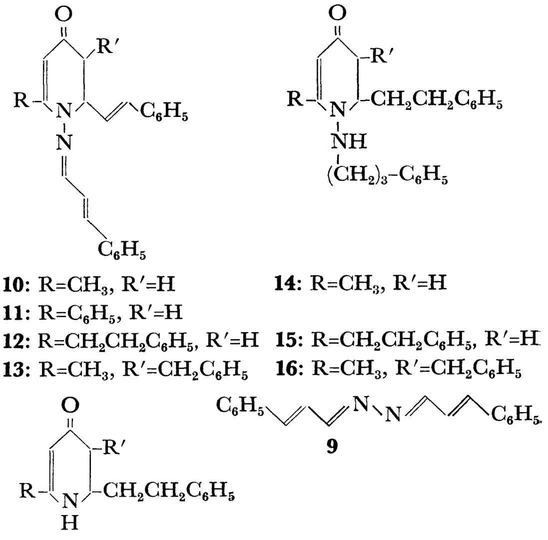
The condensation of 6-phenyl-2,4-hexanedione (**2**) with **4** gave 6-phenethyl-1-phenyl-2-styryl-2,3-dihydro-4-pyridone (**6**) and its isomer, 3-benzyl-6-methyl-1-phenyl-2-styryl-2,3-dihydro-4-pyridone (**7**) in 13.5 and 4.5% yields respectively. Thus, in the reaction of **2** with benzylidenaniline, C-1 methyl was more reactive than the C-5 methylene of **2**.[1]

It was shown that the dihydropyridone ring is not changed in ethanol during catalytic reduction with a palladium charcoal or a platinum oxide catalyst,[3] but in acetic acid it is hydrogenated by a platinum oxide catalyst to piperidone or piperidinol.[4] These results suggested that when dihydropyridones with a styryl group at the C-2 position are treated with platinum oxide in ethanol, dihydropyridones with a phenethyl group at C-2 may be produced.

The catalytic hydrogenation of **5** gave the expected product, 6-methyl-2-phenethyl-1-phenyl-2,3-dihydro-4-pyridone (**8**) in a poor yield. The ultraviolet spectrum of **8** showed an absorption maximum at 324 mμ which is attributable to the α,β-unsaturated β-aminoketone chromophore, but the absorption at 254 mμ, corresponding to that of the cinnamyl group, disappeared. This proved the formation of **8**.

On the basis of these results and those described in a previous paper,[4] the condensation products of β-diketones with cinnamaldehyde azine (**9**) can be said to be, in fact, catalytically hydrogenated to 2-phenethyl-dihydropyridones.

The condensation of one mole of **1** with a half mole of **9** in the presence of three moles of potassium amide in liquid ammonia gave 1-cinnamylidenamino-6-methyl-2-styryl-2,3-dihydro-4-pyridone(**10**) in a 14.0% yield. Under the same conditions, from benzoylacetone (**3**) and **9**, 1-cinnamylidenamino-6-phenyl-2-styryl-2,3-dihydro-4-pyridone(**11**) was obtained in a poor yield. Similarly, **2** condensed


10: $R=CH_3$, $R'=H$

11: $R=C_6H_5$, $R'=H$

12: $R=CH_2CH_2C_6H_5$, $R'=H$

13: $R=CH_3$, $R'=CH_2C_6H_5$

14: $R=CH_3$, $R'=H$

15: $R=CH_2CH_2C_6H_5$, $R'=H$

16: $R=CH_3$, $R'=CH_2C_6H_5$

9

17: $R=CH_3$, $R'=H$

21: $R=CH_2CH_2C_6H_5$, $R'=H$

22: $R=CH_3$, $R'=CH_2C_6H_5$

Fig. 3.

---

[3] N. Sugiyama, M. Yamamoto and C. Kashima, unpublished data.

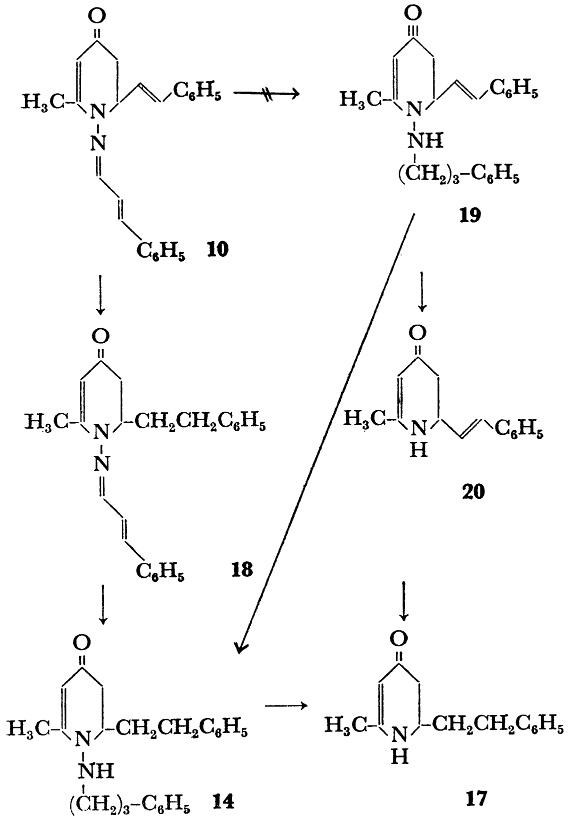
[4] C. Kashima, M. Yamamoto and N. Sugiyama, This Bulletin, **42**, 2690 (1969).

with **9** to give 1-cinnamylidenamino-6-phenethyl-2-styryl-2,3-dihydro-4-pyridone (**12**) and its isomer, 3-benzyl-1-cinnamylidenamino-6-methyl-2-styryl-2,3-dihydro-4-pyridone (**13**) in 15.7 and 5.0% yields respectively. In this reaction of **9**, C-1 is more reactive than the C-5 of **2**.

The structures of **10** and **12** were confirmed by a study of their spectral data and by elemental analyses, but those of both **11** and **13** had to be assigned only from the spectral data.

Compounds **10**, **12**, and **13** were hydrogenated with platinum oxide in ethanol. The hydrogenation of **10** gave 6-methyl-2-phenethyl-1-(3-phenylpropylamino)-2,3-dihydro-4-pyridone (**14**) and 6-methyl-2-phenethyl-2,3-dihydro-4(1*H*)-pyridone (**17**) in 19 and 52% yields respectively. The structures of **14** and **17** were confirmed by studying their spectral data.

In the hydrogenation of **10**, many intermediate products were expected to be obtained, as is illustrated in Scheme 1. The hydrogenation of **10** was interrupted after about 1.7 mol of hydrogen to **10** had been absorbed. From this reaction mixture, 1-cinnamylidenamino-6-methyl-2-phenethyl-2,3-dihydro-4-pyridone (**18**) and **14** were obtained, both in 29% yields, accompanied by a trace of **17**, but neither **19** nor **20** was detected. The further hydrogenation of **18** with platinum oxide in ethanol gave **14** and **17**, while the same treatment of **14** gave only **17**. These results suggest that the hydrogenation proceeds through the route **10**→**18**→**14**→**17**.



Scheme 1.
Intermediates of the Hydrogenation of **10** to **17**

The hydrogenation of **12** gave **15** and **21**, and that of **13** gave **16** and **22**. The structures of **15**, **16**, **21**, and **22** were confirmed by a study of their spectral data,[5,6] and, in the case of **21**, by elemental analyses.

By the use of the procedure described above, dihydropyridones with aliphatic substituents can be synthesized. This procedure consists of simple reaction steps, so that it can be a general method of dihydropyridone synthesis.

Experimental

The Condensation Reaction in Liquid Ammonia. General Procedure. In a 500-m*l*, three necked flask, about 300 m*l* liquid ammonia was placed. A small amount of sodium or potassium was added and dissolved completely. Into the resulting blue solution a catalytic amount of ferric chloride was stirred, and then 0.09 g atom of sodium or potassium in small portions. The color of the solution changed from blue to dark gray within 60—90 min. To this solution 0.03 mol of β-diketone in 30 m*l* of anhydrous ether was added in small portions. After stirring for an hour, 0.03 mol of cinnamylidenaniline (**4**) or cinnamaldehyde azine (**9**) in 50 m*l* of anhydrous ether was added in small portions. After stirring for four hours at −33°C, the reaction mixture was neutralized with solid ammonium chloride (8.0 g). The liquid ammonia was evaporated rapidly on a water bath, and 100 m*l* of ether was added gradually to the residue. The ethereal layer was separated. The ether-insoluble layer was dissolved in 150 m*l* of dilute hydrochloric acid, and then extracted with chloroform. The ether and chloroform layers were washed with water and dried over anhydrous sodium sulfate. The ether and chloroform were evaporated to give the same condensation product.

6-Methyl-1-phenyl-2-styryl-2,3-dihydro-4-pyridone (5). According to the general procedure, 0.03 mol of **1** and 0.03 mol of **4** were allowed to react in the presence of 0.09 mol of sodium amide. The reaction mixture was chromatographed on a silica gel (Merck 7734, 0.05—0.2 mm) column with a benzene - ethyl acetate (2 : 1 v/v) mixture. A fraction that showed a brownish green ferric chloride test was collected, worked up as usual, and recrystallized from benzene to give 0.39 g (4.5%) of **5** as pale yellow prisms; mp 62—63°C.

Found: C, 83.05; H, 6.80; N, 4.87%. Calcd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84%.

IR(KBr): 1630 (ν C=O), 1550 cm^{-1} (ν C=C).

UV: λ_{max}^{EtOH} mμ(ε): 254 (16900), 286 (5400), 295 (6750) and 325 (17100).

NMR(in $CDCl_3$)(τ): 8.18 (singlet, 3H, C-6 methyl protons), 7.67—6.78 (multiplet, 2H, C-3 methylene

---

[5] H. E. A. Kramer, *Ann. Chem.*, **696**, 15 (1966).

[6] C. Kashima, M. Yamamoto and N. Sugiyama, *J. Chem. Soc., C*, **1970**, 111.

protons), 5.60—5.30 (multiplet, 1H, C-2 methine proton), 4.81 (singlet, 1H, C-5 olefin proton), 3.63 (doublet, 1H, β-olefin proton of C-2 styryl group), and 2.77—2.50 (11H, multiplet, aromatic and α-olefin proton of C-2 styryl group).

The reaction of 0.015 mol of **1** with equimolar **4** was carried out in the presence of 0.03 mol of potassium amide by the general procedure. The purification of the reaction product by column chromatography gave 0.25 g (5.8%) of **5**. The reaction of 0.04 mol of **1**, 0.04 mol of **4**, and 0.12 mol of potassium amide yielded 1.52 g (13.1%) of **5**.

6-Phenethyl-1-phenyl-2-styryl-2,3-dihydro-4-pyridone (6). The reaction of 0.015 mol of **2** with an equimolar amount of **4** was carried out in the presence of 0.045 mol of potassium amide by the general procedure. By the chromatography of the reaction product on a silica-gel (Merck 7734) column with a benzene - ethyl acetate (2 : 1 v/v) mixture, a fraction with the R_f-value of 0.27 (on the thin-layer chromatography of silica-gel (Wako gel B-5) with benzene - ethyl acetate (2 : 1 v/v)) was collected. When this fraction was worked up by the usual procedure and recrystallized from benzene, 764 mg (13.5%) of **6** were afforded as colorless plates; mp 174—176°C.

Found: C, 85.64; H, 6.73; N, 3.75%. Calcd for $C_{27}H_{25}NO$: C, 85.45; H, 6.64; N, 3.69%.

IR(KBr): 1630 (ν C=O), 1550 (ν C=C), and 700 cm^{-1} (phenyl).

UV: $\lambda_{\max}^{\mathrm{EtOH}}$ mμ(ε): 254 (19800), 285 (4900), 295 (5000) and 331 (17700).

NMR(in $CDCl_3$)(τ): 7.64—7.16 (multiplet, 4H, ethylene protons of the C-6 phenethyl group), 7.78—6.76 (multiplet, 2H, C-3 methylene protons), 5.73—5.45 (multiplet, 1H, C-2 methine proton), 4.70 (singlet, 1H, C-5 olefin proton), 3.60 (doublet, 1H, β-olefin proton of the C-2 styryl group), and 3.20—2.57 (multiplet, 16H, aromatic protons and α-olefin proton of the C-2 styryl group).

3-Benzyl-6-methyl-1-phenyl-2-styryl-2,3-dihydro-4-pyridone (7). Compound **7** was obtained from the same reaction mixture as **6**. By column chromatography with benzene - ethyl acetate (2 : 1 v/v), **7** was eluted ahead of **6**. On silica-gel (Wako gel B-5) thin-layer chromatography with benzene - ethyl acetate (2 : 1 v/v), **7** showed an R_f-value of 0.35, while that of **6** was 0.27. The fraction containing **7** was concentrated and recrystallized from ethyl acetate to give 255 mg (4.5%) of **7** as pale yellow prisms; mp 155—156°C.

Found: C, 85.49; H, 6.66; N, 3.79%. Calcd for $C_{27}H_{25}NO$: C, 85.45; H, 6.64; N, 3.69%.

IR(KBr): 1635 (ν C=O), 1560 (ν C=C) and 705 cm^{-1} (phenyl).

UV: $\lambda_{\max}^{\mathrm{EtOH}}$ mμ(ε): 253 (18300), 285 (4950), 294 (5460) and 328 (17900).

NMR(in $CDCl_3$)(τ): 8.10 (singlet, 3H, C-6 methyl protons), 7.60—6.64 (multiplet, 3H, C-3 methine and methylene protons of the C-3 benzyl group), 5.94 (quartet, 1H, C-2 methine proton), 4.80 (singlet, 1H, C-5 olefin proton), 3.98—3.31 (multiplet, 1H, β-olefin proton of the C-2 styryl group), and 2.85—2.55 (multiplet, 16H, α-olefin proton of the C-2 styryl group, and aromatic protons).

6-Methyl-2-phenethyl-1-phenyl-2,3-dihydro-4-pyridone (8). A mixture of 30 m*l* of ethanol, 150 mg of **5**, and 100 mg of platinum oxide was stirred under the atmospheric pressure of hydrogen. After absorbing 49 m*l* of hydrogen, the reaction mixture was treated in the usual manner and then purified by chromatography on a silica-gel (Merck 7729, 0.08 mm) column, using a benzene - ethyl acetate (2 : 1 v/v) mixture. A fraction with an R_f-value of 0.25 was collected on silica-gel (Wako gel B-5) thin-layer chromatography, using a benzene - ethyl acetate (2 : 1 v/v) mixture; this value was different from that of **5**, 0.16. However, this fraction was proved to contain a trace of **8** and 111 mg (74%) of recovered **5**.

Syntheses of 1-Cinnamylidenamino-2,3-dihydro-4-pyridones. According to the general procedure, 1-cinnamylidenamino-2,3-dihydro-4-pyridones were prepared from 0.015 mol of β-diketone and 0.015 mol of cinnamaldehyde azine (**9**). The crude product was chromatographed on a silica-gel (Merck 7734) column, using a benzene - ethyl acetate (4 : 1 v/v) mixture. A fraction which showed a green color with ferric chloride was collected and then again chromatographed on a silica-gel (Merck 7729) column, using a benzene - ethyl acetate (2 : 1 v/v) mixture. A fraction which showed a green color with ferric chloride was collected, concentrated, and recrystallized from the appropriate solvent to yield pure dihydropyridones, **10**, **11**, **12** and **13**.

1-Cinnamylidenamino-6-methyl-2-styryl-2,3-dihydro-4-pyridone (10). Compound **10** was prepared from 0.015 mol of **1** and 0.015 mol of **9**. Yield, 0.70 g (14.0%); yellow prisms (recrystallized from benzene); mp 185—186°C.

Found: C, 80.57; H, 6.61; N, 8.08%. Calcd for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.48; N, 8.10%.

IR(KBr): 1640 (ν C=O), 1590 (ν C=N) and 1555 cm^{-1} (ν C=C).

UV: $\lambda_{\max}^{\mathrm{EtOH}}$ mμ(ε): 238 (18700), 246 (21500), 256 (22000), 286 (16000), 372 (40400) and 382 (40400).

NMR(in $CDCl_3$)(τ): 7.70 (singlet, 3H, C-6 methyl protons), 7.42 (quartet, 1H, C-3 methylene proton, ABX type), 6.85 (quartet, 1H, C-3 methylene proton, ABX type), 4.95 (multiplet, 1H, C-2 methine proton, ABX type), 4.85 (singlet, 1H, C-5 olefin proton), 4.04 (quartet, 1H, α-olefin proton of the C-2 styryl group), 3.67 (doublet, 1H, β-olefin proton of the C-2 styryl group), 3.15 (multiplet, 2H, β′-, γ′-olefin protons of the 1-cinnamylidenamino group), and 2.76—2.30 (multiplet, 11H, α′-olefin proton of the 1-cinnamylidenamino group and aromatic protons).

1-Cinnamylidenamino-6-phenyl-2-styryl-2,3-dihydro-4-pyridone (11). Compound **11** was prepared from 0.015 mol of **3** and an equimolar amount of **9** in a poor yield (yellow solid). UV spectrum of **11**: $\lambda_{\max}^{\mathrm{EtOH}}$ 251, 295 and 378 mμ.

1-Cinnamylidenamino-6-phenethyl-2-styryl-2,3-dihydro-4-pyridone (12). From 0.015 mol of **2** and an equimolar amount of **9**, 1.02 g (15.7%) of **12** were prepared. Yellow prisms; mp 131—134°C (recrystallized from ethanol).

Found: C, 83.11; H, 6.65; N, 6.43%. Calcd for $C_{30}H_{28}N_2O$: C, 83.30; H, 6.53; N, 6.48%.

IR(KBr): 1635 (ν C=O), 1580 (ν C=N) and 1550 cm^{-1} (ν C=C).

UV: $\lambda_{\max}^{\mathrm{EtOH}}$ mμ(ε): 247 (23100), 256 (22400), 286 (15700), 293 (14400), 373 (42300) and 385 (42500).

NMR(in $CDCl_3$)(τ): 7.00 (singlet, 3H, ethylene protons of the C-6 phenethyl group), 6.64—7.58 (ABX type double quartet, 2H, C-3 methylene protons, $J_{AB}=16.5$, $J_{AX}=7.2$ and $J_{BX}=1.5$ Hz), 4.85 (multiplet, 1H, C-2 methine proton), 4.83 (singlet, 1H, C-5 olefin proton), 4.00 (quartet, 1H, α-olefin proton, $J_{\alpha X}=4.5$ Hz), 3.58 (doublet, 1H, β-olefin proton, $J_{\alpha\beta}=15.7$ Hz), 3.10 (multiplet, 2H, β'- and γ'-olefin protons of the 1-cinnamylidenamino group), and 2.75—2.30 (multiplet, 16H, α'-olefin proton of the 1-cinnamylidenamino group and aromatic protons).

3-Benzyl-1-cinnamylidenamino-6-methyl-2-styryl-2,3-dihydro-4-pyridone (13). Compound **13** was obtained from the same reaction mixture as **12**. The fraction which was eluted first showed an R_f-value of 0.21 on silica-gel (Wako gel B-5) thin-layer chromatography with a benzene - ethyl acetate (10 : 1 v/v) mixture. However, **12** showed an R_f-value of 0.10. When it was worked up as usual, 0.32 g (5.0%) of **13** was yielded as a viscous yellow oil.

IR(liquid film): 1630 (ν C=O), 1585 (ν C=N) and 1550 cm^{-1} (ν C=C).

Catalytic Hydrogenation of 10. A solution of 390 mg of **10** in 50 m*l* of ethanol was hydrogenated with 100 mg of platinum oxide at room temperature and under an atmospheric pressure. After absorbing about 105 m*l* of hydrogen (calculated 111 m*l*), the absorption of hydrogen almost ceased. After the catalyst had then been filtered off, the ethanol solution was worked up as usual. It was chromatographed on a silica-gel (Merck 7729) column with a benzene - ethyl acetate (1: 1 v/v) mixture. Two fractions which showed brown and green colors with ferric chloride were collected. The brown-colored fraction was again chromatographed on a silica-gel (Merck 7729) column with a benzene - ethyl acetate (2 : 1 v/v) mixture to give 76 mg (19%) of 6-methyl-2-phenethyl-1-(3-phenylpropylamino)-2,3-dihydro-4-pyridone (**14**) as a yellow oil.

NMR(in $CDCl_3$)(τ): 8.00 (singlet, 3H, methyl protons), 8.43—7.00 (multiplet, 12H, C-3 methylene protons and ethylene protons of the C-2 phenethyl group and trimethylene protons of the 1-(3-phenylpropylamino-group), 6.54—6.20 (multiplet, 1H, C-2 methine proton), 6.05 (broad singlet, 1H, NH; this signal disappeared upon treatment with D_2O[2]), 5.17 (singlet, 1H, C-5 olefin proton), and 2.89—2.55 (multiplet, 10H, aromatic protons).

The fraction which showed a green color with ferric chloride was again chromatographed on a silica-gel (Merck 7729) column with a benzene - ethyl acetate (1 : 2 v/v) mixture to give 128 mg (52%) of 6-methyl-2-phenethyl-2,3-dihydro-4(1*H*)-pyridone (**17**) as colorless needles; mp 143—145°C.

Found: C, 77.93; H, 8.08; N, 6.45%. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51%.

IR(KBr): 3220 (ν NH), 1600 (ν C=O) and 1575 cm^{-1} (ν C=C).

UV: λ_{max}^{EtOH} mμ(ε): 314 (15400) and $\lambda_{max}^{HCl/EtOH}$ 307 (10300).

NMR(in $CDCl_3$)(τ): 8.10 (singlet, 3H, C-6 methyl protons), 8.02—7.12 (multiplet, 6H, C-3 methylene protons and ethylene protons of the C-2 phenethyl group), 6.50—6.20 (multiplet, 1H, C-2 methine proton), 5.10 (singlet, 1H, C-5 olefin proton), 4.73 (broad singlet, 1H, NH), and 2.85—2.70 (multiplet, 5H, aromatic protons).

According to the same procedure, from the compound **12**, **15** and **21** were obtained, and from the compound **13**, **16** and **22** were prepared. The compounds **15, 16** and **22** could not be purified well, so the structures of these compounds were confirmed only by the spectral data.

2,6-Diphenethyl-1-(3-phenylpropylamino)-2,3-dihydro-4-pyridone (15). From 1.40 g of **12**, 380 mg (26.8%) of **15** and 264 mg (26.7%) of **21** were obtained.

IR of **15** (liquid film): 3250 (ν NH), 1610 (ν C=O) and 1540 cm^{-1} (ν C=C).

UV: λ_{max}^{EtOH} 329 mμ, $\lambda_{max}^{HCl/EtOH}$ 325 mμ.

NMR(in $CDCl_3$)(τ): 8.45—6.95 (multiplet, 16H), 6.96—6.69 (broad singlet, 1H, NH), 6.50—6.18 (multiplet, 1H, C-2 methine proton), 5.10 (singlet, 1H, C-5 olefin proton), 2.79, 2.80, 2.82 (singlets, 15H, aromatic protons).

2,6-Diphenethyl-2,3-dihydro-4(1*H*)-pyridone (21). Mp 144—146°C; colorless needles.

Found: C, 82.46; H, 7.55; N, 4.54%. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59%.

IR(KBr): 3250 (ν NH), 1605 (ν C=O) and 1570 cm^{-1} (ν C=C).

UV: λ_{max}^{EtOH} mμ(ε): 316 (15000), $\lambda_{max}^{HCl/EtOH}$ 310 (10200).

3-Benzyl-6-methyl-2-phenethyl-1-(3-phenylpropylamino)-2,3-dihydro-4-pyridone (16). From 400 mg of **13**, 158 mg of **16** were obtained. $FeCl_3$ test: brown.

IR(liquid film): 3250 (ν NH), 1615 (ν C=O), and 1555 cm^{-1} (ν C=C).

From the above reaction mixture, a trace of 3-benzyl-6-methyl-2-phenethyl-2,3-dihydro-4(1*H*)-pyridone (**22**) was obtained. $FeCl_3$ test: green.

UV: λ_{max}^{EtOH} 318 mμ, $\lambda_{max}^{HCl/EtOH}$ 310 mμ.

1-Cinnamylidenamino-6-methyl-2-phenethyl-2,3-dihydro-4-pyridone (18). A solution of 2.0 g of **10** in 50 m*l* of ethanol was hydrogenated with 150 mg of platinum oxide. After the mixture had absorbed about 24 m*l* (calculated 56 m*l*) of hydrogen, absorption was stopped. After the catalyst had been filtered off and the ethanol solution worked up as usual, the reaction product was purified by a column chromatography similar to that described above to afford 575 mg (29%) of **18** as a viscous orange oil.

UV: λ_{max}^{EtOH} 244, 249, and 340 mμ.

NMR(in $CDCl_3$)(τ): 7.91 (singlet, 3H, C-6 methyl protons), 7.78—7.00 (multiplet, 6H, ethylene protons of the phenethyl group and C-3 methylene protons), 6.15—5.75 (multiplet, 1H, C-2 methine proton), 5.01 (singlet, 1H, C-5 olefin proton), 3.52 (triplet, 1H, β'-olefin proton of the 1-cinnamylidenamino group) and 2.90—2.60 (multiplet, 12H, α'-, γ'-olefin protons of the 1-cinnamylidenamino group and aromatic protons).

As well as **18**, 460 mg (29%) of **14** and a trace of **17** were afforded.

Hydrogenation of 18. Compound **18** (120 mg) was hydrogenated with 50 mg of platinum oxide in 30 m*l* of ethanol. After about 20 m*l* of hydrogen had been absorbed, the absorption of hydrogen was stopped. The reaction mixture was then treated as usual; we thus obtained **14** and **17** which were identified with authentic samples by means of thin-layer chromatography.

Hydrogenation of 14 to 17. In the presence of 100 mg of platinum oxide in 50 m*l* of ethanol, 400 mg of **14** were hydrogenated. After about 50 m*l* of hydrogen had been absorbed, the absorption of hydrogen almost ceased. When the reaction mixture was worked up as usual it gave **17**, which was identified with an authentic sample by means of thin-layer chromatography.