Synthesis of Methylpyridine and 1, 8-Naphthylidine Derivatives

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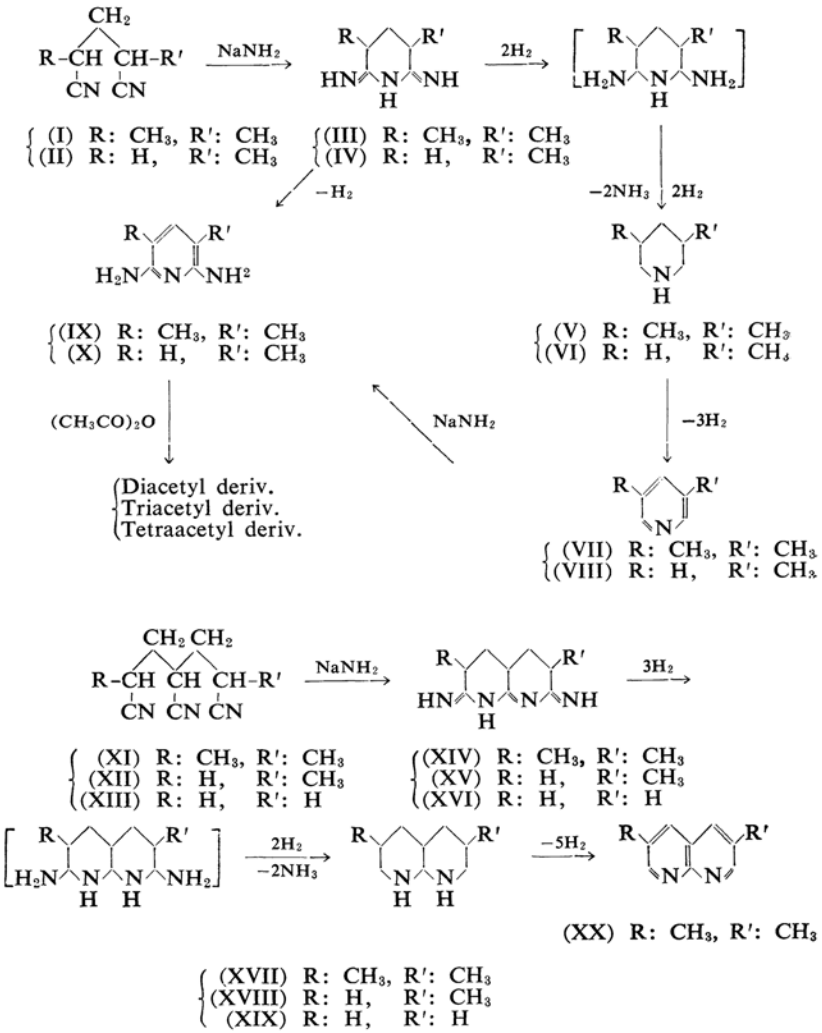
(Received January 18, 1962)

Usually, pyridine and 1, 8-naphthylidine derivatives are prepared from carbonyl compounds and from α-aminopyridines respectively[1,2]. The present paper describes a synthesis of those derivatives from aliphatic dinitriles[3] or from trinitriles accomplished through the scheme shown below:

The ring-closure reactions of dinitriles (I and II) and trinitriles (XI, XII and XIII) were carried out according to the techniques of Elvidge[4] for succinonitrile, using sodium amide to give glutaroimidine derivatives (III and IV) or diimino-1, 8-naphthylidine derivatives (XIV, XV and XVI).

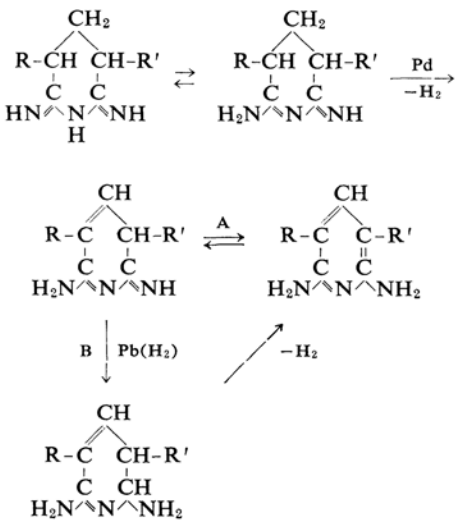


1) T. Matsukawa et al., "Dai Yūki Kagaku", Vol. 16, Asakura Shoten, Tokyo (1959), pp. 390—391.
2) C. F. Allen, *Chem. Revs.*, **47**, 275 (1950).
3) T. Takata and M. Taniyama, *Kōbunshi Kagaku*, **16**, 693 (1959).
4) J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, **1954**, 442.

Those cyclic imidine-type compounds (III, IV, XIV, XV and XVI) were hydrogenated in an alcoholic solution with sodium to give piperidine derivatives (V and VI) or decahydro-1,8-naphthylidine derivatives (XVII, XVIII and XIX), the imino groups were eliminated almost quantitatively as ammonia, as in the case of α-aminopyridine[5].

Dehydrogenations of the cyclic compounds (III, IV, V, VI and XVII) were carried out by treating them with a palladium catalyst to yield α, α'-diaminopyridines (IX and X), methylpyridines (VII and VIII), or dimethyl-1,8-naphthylidine (XX). Monomethyl-α, α'-diaminopyrine (X) was also obtained from VIII by treating it with sodium amide[6]; between the infrared spectra of the X derived from VIII and that derived from IV, no difference could be detected, as is shown in Fig. 1.

Therefore, the formation of α, α'-diaminopyridines from glutaroimidines suggests the possibility of the mechanism shown below, in which reaction B may be more probable than A.



As another route for the synthesis of 1,8-naphthylidines, we followed the procedure of Reissert[7,8] except for the preparation of the δ-carboxyheptamethylene diamines, which had been prepared from γ-bromopropylphthalimide and diethyl malonate by Reissert, but which we derived from diethyl malonate and acrylonitrile or methacrylonitrile. This scheme is shown below.

5) A. E. Tschitschibabin and M. P. Gertschuk, *Ber.*, **63**, 1153 (1930).
6) A. E. Tschitschibabin and Seide, *Chem. Zentr.*, **1915**, I. 1065.
7) A. Reissert, *Ber.*, **26**, 2137 (1893).
8) A. Reissert, ibid., **27**, 980 (1894).

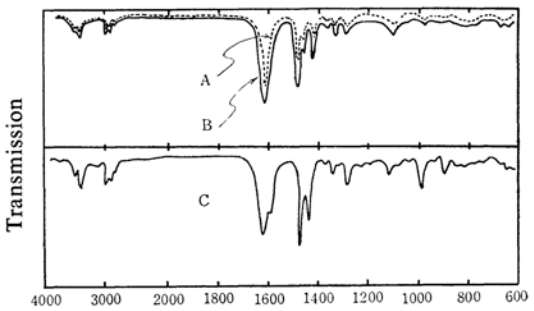
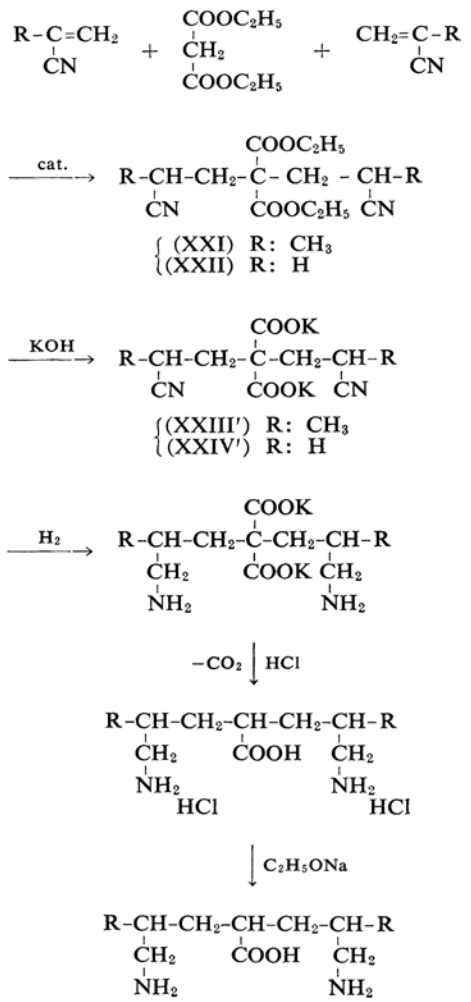
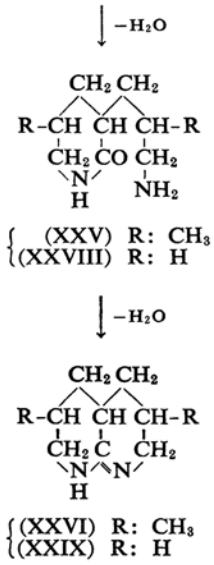


Fig. 1. Infrared spectra of 2,6-diamino-pyridine derivatives in chloroform.

A: 2,6-Diamino-3-methylpyridine (X), derived from 3-methylpyridine (VIII)
B: 2,6-Diamino-3-methylpyridine (X), derived from 2-methylglutaroimidine (IV)
C: 2,6-Diamino-3,5-dimethylpyridine (IX), derived from α, α'-Dimethylglutaroimidine (III)





In this route γ,γ-diethoxycarbonylpimeronitriles (XXI and XXII) were prepared from diethyl malonate and acrylonitrile (by the use of potassium hydroxide[9] as a catalyst, although Koelsh[10] used sodium ethoxide for this purpose) or from methacrylonitrile (by using sodium ethoxide).

The compounds XXI and XXII were then saponified with potassium hydroxide to potassium salts (XXIII' and XXIV'), which were hydrogenated in the presence of a Raney-nickel catalyst to diaminodicarboxylic acid derivatives. When these diaminodicarboxylic acids were treated with concentrated hydrochloric acid, decarboxylation occurred and the hydrochlorides of diaminomonocarboxylic acids were formed; these hydrochlorides were not isolated but were treated with sodium ethoxide in ethanol to liberate diaminomonocarboxylic acids. These diaminomonocarboxylic acids were pyrolyzed to lactam derivatives (XXV and XXVIII), which also were not isolated but which were identified by infrared spectra and by the formation of picrates.

By the pyrolysis of XXV and XXVIII, the octahydro-1, 8-naphthylidines (XXVI and XXIX) reported by Reissert[7,8] were not obtained, but dimethyltetrahydro-1, 8-naphthylidine (XXVII) and hexahydro-1, 8-naphthylidine (XXX) were obtained. This fact suggests that the dehydrogenation[11] with air was accompanied with dehydration in order to give XXVI and XXIX in the thermal treatments of XXV and XXVIII.

In Fig. 2 below, the infrared spectra of dimethyldecahydro-, dimethyltetrahydro- and dimethyl-1, 8-naphthylidine are compared with one other.

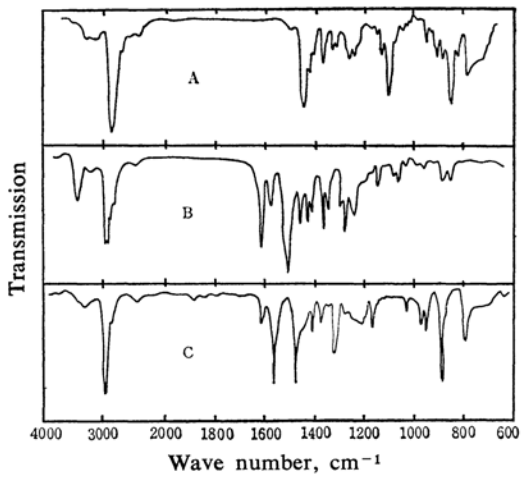


Fig. 2. Infrared spectra of 3, 6-dimethyl-1, 8-naphthylidine derivatives in chloroform.
A: 3, 6-Dimethyldecahydro-1, 8-naphthylidine (XVII)
B: 3, 6-Dimethyltetrahydro-1, 8-naphthylidine (XXVII)
C: 3, 6-Dimethyl-1, 8-naphthylidine (XX)

Experimental

α,α'-Dimethylglutaroimidine (III). — α,α'-Dimethylglutaronitrile (I)[3] (43 g.) was added to a cooled solution of sodium amide (30 g.) in formamide (258 ml.); after standing for 2 days at room temperature, this solution gave a crystalline product, which was collected by filtration, washed with *n*-propanol, ethyl acetate, and ether, and recrystallized from absolute ethanol, affording III (41.0 g., 83.7%) as colorless prismatic needles, m. p., 209~210°C (decomp.).

Found: C, 59.81; H, 9.39; N, 30.04. Calcd. for $C_7H_{13}N_3$: C, 60.40; 9.41; N, 30.19%.

α-Methylglutaroimidine (IV). — By a method similar to that described above, IV was obtained from α-methylglutaronitrile (II)[3] (37 g.) and sodium amide (26 g., in 222 ml. of formamide) in the form of colorless prismatic needles, m. p., 154~155°C (decomp.) (from absolute ethanol); yield. 30.0 g. (70.1%).

Found: C, 57.71; H, 8.88; N, 30.31. Calcd. for $C_6H_{11}N_3$: C, 57.57; H, 8.86; N, 35.57%.

3, 5-Dimethylpiperidine (V).—Into a solution of III (7 g.) in absolute ethanol (100 ml.) on an oil bath at 130~140°C were alternately stirred sodium (98 g.) and absolute ethanol in small portions. Then the reaction mixture was submitted to steam distillation. The distillate was acidified with hydrochloric acid, concentrated, and treated with excess sodium hydroxide to liberate the free base, from which 4.6 g. (80.7%) of V was obtained by distillation; b. p., 144°C, d_4^{20} 0.8532, n_D^{20} 1.4560.

During this reaction the evolved gas was bubbled

9) H. Zahn and P. Schäfer, ibid., **92**, 736 (1959).
10) C. F. Koelsch, *J. Am. Chem. Soc.*, **65**, 2458 (1943).
11) A. V. Topchiyev et al., *Chem. & Ind.*, **1960**, 184.

through aqueous sulfuric acid; by titration of this sulfuric acid solution, 1.45 g. of ammonia was detected. (The calculated amount of ammonia from 7 g. of III is 1.71 g.).

The Picrate of V.—M. p., 184°C (from water). Found: C, 45.60; H, 5.35; N, 16.22. Calcd. for $C_{13}H_{18}N_4O_7$: C, 45.61; H, 5.30; N, 16.37%.

3-Methylpiperidine (VI).—By a method similar to that described above, VI was obtained from IV (7 g. in 100 ml. of absolute ethanol), sodium (98 g.) and absolute ethanol (600 ml.). B. p., 125~126°C, d_4^{20} 0.8570, n_D^{20} 1.4506; yield, 3.2 g. (58.2%).

In this reaction 1.68 g. of eliminated ammonia was detected. (The calculated amount of ammonia for 7 g. of IV is 1.90 g.).

The Picrate of VI.—M. p., 105°C (from water). Found: C, 44.08; H, 4.92; N, 17.14. Calcd. for $C_{12}H_{16}N_4O_7$: C, 43.90; H, 4.91; N, 17.07%.

3, 5-Dimethylpyridine (VII).—In an atmosphere of nitrogen, compound V (0.5 g.) was heated at 230°C for 5 hr. in the presence of a palladium catalyst (0.2 g.). Then 0.35 g. (74.5%) of VII was obtained by distillation; b. p., 168~171°C, d_4^{20} 0.9096, n_D^{20} 1.4501.

The Picrate of VII.—M. p., 242~243°C (decomp.) (from water). Found: C, 46.26; H, 3.61; N, 16.44. Calcd. for $C_{13}H_{12}N_4O_7$: C, 46.43; H, 3.60; N, 16.66%.

3-Methylpyridine (VIII).—By a method similar to that described above, 0.35 g. (74.5%) of VIII was obtained from VI (0.5 g.). B. p., 142°C, d_4^{20} 0.9556, n_D^{20} 1.5053.

The Picrate of VIII.—M. p., 149~150°C (from ethyl acetate). Found: C, 44.73; H, 3.23; N, 17.35. Calcd. for $C_{12}H_{10}N_4O_7$: C, 44.73; H, 3.13; N, 17.39%.

2, 6-Diamino-3, 5-dimethylpyridine (IX).—In an atmosphere of nitrogen, compound III (1 g., in 4 ml. of diphenyl ether) was heated at 300°C for 11 hr. in the presence of a palladium catalyst (0.6 g.). The reaction mixture was then dissolved in ether and shaken with dilute hydrochloric acid. The aqueous layer was treated with sodium hydroxide to liberate the basic product, which was extracted with ether. The crystals obtained after evaporation of the ether were recrystallized from benzene to give IX, in the from of colorless needles; m. p., 186~187°C, yield, 0.3 g. (30.6%).

Found: C, 61.62; H, 8.18; N, 31.00. Calcd. for $C_7H_{11}N_3$: C, 61.28; H, 8.08; N, 30.63%.

Tetraacetyl-2,6-diamino-3,5-dimethylpyridine.—Compound IX (21 mg.) was treated with acetic anhydride (1 ml.) at 170°C for 1 hr. in a sealed glass tube. After removal of the acetic acid and unreacted acetic anhydride by distillation, the residue was recrystallized from benzene to give the tetraacetyl derivative of IX as colorless crystals; m. p., 149°C; yield, 20.7 mg. (44.2%).

Found: N, 13.77. Calcd. for $C_{15}H_{19}N_3O_4$: N, 13.76%.

Diacetyl-2, 6-diamino-3, 5-dimethylpyridine. — Compound IX (17 mg.) was treated with acetic anhydride (1 ml.) at 95°C for 1 hr. to give the diacetyl derivative of IX in the form of colorless crystals; m. p., 197°C; yield, 5 mg. (18.2%).

Found: N, 18.43. Calcd. for $C_{11}H_{15}N_3O_2$: N, 18.99%.

2, 6-Diamino-3-methylpyridine (X). — *a) By the Tschitschibabin-Seide Method*[6]. — Compound VIII (12.2 g.) was treated with sodium amide (16 g.) in tetraline (16 g.) at 150~153°C for 4 hr. and thereafter at 198~200°C for 17 hr. The reaction mixture was then poured into water and extracted with benzene. From the benzene extract X was obtained in the form of colorless plates; m. p., 156~157°C (from benzene); yield, 2.5 g. (15.5%).

Found: C, 58.48; H, 7.31; N, 34.54. Calcd. for $C_6H_9N_3$: C, 58.51; H, 7.37; N, 34.12%.

b) By the Dehydrogenation of IV.—By a method similar to that described for IX, X was obtained from IV (0.5 g.) as colorless plates; m. p., 156~157°C (from benzene), undepressed on admixture with the specimen derived from VIII; yield, 0.15 g. (30.6%).

Triacetyl-2, 6-diamino-3-methylpyridine.—By a method similar to that described for tetraacetyl-2, 6-diamino-3, 5-dimethylpyridine, compound X (99.8 mg.) was treated with acetic anhydride (3 ml.) at 170~180°C for 3 hr., giving the triacetyl derivative of X in the from of colorless crystals; m. p., 142~144°C (from benzene); yield, 53.4 mg. (26.4%).

Found: N, 16.72. Calcd. for $C_{12}H_{15}N_3O_3$: N, 16.86%.

Diacetyl-2, 6-diamino-3-methylpyridine. — Compound X (100.3 mg.) was treated with acetic anhydride (2 ml.) at 90~100°C for 1 hr. to give the diacetyl derivative of X as colorless crystals; m. p., 220~221°C (from petroleum ether); yield, 78.1 mg. (46.4%).

Found: N, 20.39. Calcd. for $C_{10}H_{13}N_3O_2$: N, 20.28%.

3, 6-Dimethyl-2, 7-diaminooctahydro-1,8-naphthylidine (XIV).—By a method similar to that described for III, XIV was obtained from 2, 4, 6-tricyano-*n*-heptane (XI)[3] (75 g.) and sodium amide (50 g., in 300 ml. of formamide) in the form of pale greenish-yellow crystals; m. p., 222~224°C (decomp.); yield, 71.6 g. (87%).

Found: C, 62.50; H, 8.46; N, 29.23. Calcd. for $C_{10}H_{16}N_4$*: C, 62.47; H, 8.39; N, 29.14%.

3-Methyl-2, 7-diiminooctahydro-1, 8-naphthylidine (XV).—By a method similar to that described for III, XV was obtained from 1, 3, 5-tricyano-*n*-hexane (XII)[3] (77 g.) and sodium amide (52 g., in 310 ml. of formamide) in the form of pale greenish yellow crystals; m. p., 204~206°C (decomp.); yield, 55.3 g. (65.0%).

Found: C, 60.26; H, 7.74; N, 31.09. Calcd. for $C_9H_{14}N_4$: C, 60.65; H, 7.92; N, 31.44%.

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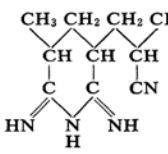
* The calculaled value for $C_{10}H_{16}N_4$ also satisfies the structure:



but this possibility can be omitted because of the lack in the infrared spectrum of the absorption band (near 2250 cm^{-1}) due to CN.

2, 7-Diiminooctahydro-1, 8-naphthylidine (XVI).—By a method similar to that described for III, XVI was obtained from 1, 3. 5-tricyano-*n*-pentane (XIII)[9] (33 g.) and sodium amide (22 g., in 123 ml. of formamide) in the form of pale greenish-yellow crystals; m. p., 205~206°C (decomp.); yield, 31.3 g. (82.3%).

Found: C, 58.25; H, 7.27; N, 34.04. Calcd. for $C_8H_{12}N_4$: C, 58.51; H, 7.37; N, 34.12%.

3,6-Dimethyldecahydro-1,8-naphthylidine (XVII). To a solution of XIV (1.5 g.) in amyl alcohol (240 ml.) was added sodium (21 g.) at 130~140°C. The reaction mixture was then submitted to steam distillation. The distillate was acidified with hydrochloric acid, concentrated, and treated with excess sodium hydroxide to liberate the free base, from which by extraction with ether, was obtained XVII in the form of colorless needles; m. p., 162~163°C (from benzene); yield, 1.0 g. (75.3%).

Found: C, 72.14; H, 11.27; N, 16.88. Calcd. for $C_{10}H_{20}N_2$: C, 72.24; H, 10.91; N, 16.85%.

In this reaction, 0.254 g. of eliminated ammonia was detected. (The calculated amount of ammonia for 1.5 g. of XIV is 0.266 g.).

The Dipicrate of XVII.—M. p., 213°C (decomp.) (prepared in ethyl acetate).

Found: C, 42.28; H, 4.23; N, 17.85. Calcd. for $C_{22}H_{26}N_8O_{14}$: C, 42.18; H, 4.18; N, 17.89%.

3-Methyldecahydro-1,8-naphthylidine (XVIII).—By a method similar to that described for XVII, XVIII was obtained from XV (7 g., in 800 ml. of amyl alcohol) and sodium (98 g.) in the form of colorless needles; m. p., 113~114°C (from benzene); yield, 4 g. (66.7%).

Found: C, 69.79; H, 11.79; N, 17.69. Calcd. for $C_9H_{18}N_2$: C, 70.07; H, 11.76; N, 18.17%.

The Dipicrate of XVIII.—M. p., 205°C (decomp.) (prepared in ethyl acetate).

Found: C, 41.47; H, 4.16; N, 17.93. Calcd. for $C_{21}H_{24}N_8O_{14}$: C, 41.18; H, 3.95; N, 18.30%.

Decahydro-1, 8-naphthylidine (XIX).—By a method similar to that described for XVII, XIX was obtained from XVI (1.2 g., in 200 ml. of amyl alcohol) and sodium (17 g.) in the form of colorless needles; m. p., 116~117°C (from benzene); yield, 0.9 g. (90.0%).

Found: C, 68.42; H, 11.50; N, 19.78. Calcd. for $C_8H_{16}N_2$: C, 68.52; H, 11.50; N, 19.98%.

The Dipicrate of XIX.—M. p., 195°C (decomp.) (prepared in ethyl acetate).

Found: C, 40.26; H, 3.93; N, 18.54. Calcd. for $C_{20}H_{22}N_8O_{14}$: C, 40.14; H, 3.71; N, 18.74%.

3, 6-Dimethyl-1, 8-naphthylidine (XX).—In an atmosphere of nitrogen, compound XVII (0.15 g., in 2 ml. of diphenyl ether) was heated at 200~270°C for 20 hr. in the presence of a palladium catalyst (0.2 g.). Thereafter, treatment by a method similar to that described for IX gave XX as light yellowish-orange, prismatic needles; m. p., 191~192°C (from benzene); yield, 0.1 g. (71.0%).

Found: C, 75.66; H, 6.36; N, 17.70. Calcd. for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; 17.71%.

The Monopicrate of XX.—M. p., 210~211°C (decomp.) (prepared in benzene).

Found: C, 49.57; H, 3.45; N, 17.90. Calcd. for $C_{16}H_{13}N_5O_7$: C, 49.62; H, 3.38; N, 18.08%.

α, α'-Dimethyl-γ, γ-dicarbethoxy-pimeronitrile (XXI).—Into a mixture of diethyl malonate (320 g., 2 mol.) and methacrylonitrile (280 g., 4.2 mol.) sodium ethoxide (11 g., in 80 g. of absolute ethanol) was stirred at 32~50°C for 8 hr. and thereafter at 80~90°C for 2 hr. After neutralization with hydrochloric acid, this mixture was poured into water to separate an oily substance, which was submitted to distillation to give XXI; b. p., 175°C/2 mmHg; m. p., 61~63°C; yield, 338 g. (57.5%).

Found: C, 61.25; H, 7.52; N, 9.47. Calcd. for $C_{15}H_{22}N_2O_4$: C, 61.20; H, 7.54; N, 9.52%.

γ, γ-Dicarbethoxy-pimeronitrile (XXII).—To a cooled and stirred mixture of diethyl malonate (187 g., 1.1 mol.), acrylonitrile (123 g., 2.3 mol.) and dioxane (233 g.) a methanolic 30% potassium hydroxide solution (10.6 ml.) was slowly added below 20°C and thereafter stirred for 2 hr. at room temperature. After neutralization with hydrochloric acid, the mixture was poured into water to separate an oily substance, which crystallized slowly and which was recrystallized from ethanol to give XXII; m. p., 60~62°C; yield, 224 g. (76.4%).

Found: C, 58.75; H, 6.90; N, 10.18. Calcd. for $C_{13}H_{18}N_2O_4$: C, 58.63; H, 6.81; N, 10.52%.

α, α'-Dimethyl-γ, γ-dicarboxy-pimeronitrile (XXIII).—A mixture of XXI (115 g.) and potassium hydroxide (55 g.) in absolute ethanol (500 ml.) was left for a few days at room temperature to precipitate the potassium salt of XXIII, which was then collected by filtration; yield, 106 g. (86.2%).

The potassium salt was dissolved in water, acidified with hydrochloric acid, and extracted with ethyl acetate to give XXIII; m. p., 134~136°C (decomp.) (from water).

Found: C, 55.27; H, 6.30; N, 11.76. Calcd. for $C_{11}H_{14}N_2O_4$: C, 55.45; H, 5.88; N, 11.76%.

γ, γ-Dicarboxypimeronitrile (XXIV).—By a method similar to that described above, from XXII (133 g.) and potassium hydroxide (65 g., in 650 ml. of absolute ethanol) was obtained the potassium salt of XXIV (135 g., 94.4%), from which XXIV was obtained after acidification with hydrochloric acid and extraction with ethyl acetate; m. p., 158°C (decomp.) (from water).

Found: C, 51.87; H, 4.90; N, 12.87. Calcd. for $C_9H_{10}N_2O_4$: C, 51.43; H, 4.80; N, 13.33%.

3-(β-Methyl-ω-amino-*n*-propyl)-5-methylpiperidone-2 (XXV).—In a 220 ml. autoclave, the potassium salt of XXIII (47.1 g., in 50% aqueous ethanol) was hydrogenated under ca. 100 atm. of hydrogen pressure below 60°C in the presence of a Raney-nickel catalyst (from 38 g. of Ni-Al alloy 50 : 50). The reaction mixture was concentrated and acidified with 300 ml. of concentrated hydrochloric acid and heated on a water bath to complete the decarboxylation. After concentration, this mixture was heated at 200°C for another 3 hr. to remove thoroughly the volatile component; the residue was then extracted with absolute ethanol. This ethanolic solution was treated with sodium ethoxide to liberate the free aminolactam (XXV) from the hydrochloride. After elimination of the sodium chloride and evaporation of the ethanol crude XXV (20 g.) was obtained, a hygroscopic sticky substance which was not purified, but in the infrared spectrum of

which there was detected the characteristic absorption band at 1670 cm^{-1} which was assigned to the lactam groups of the six-membered ring[12].

The Picrate of XXV.—M. p., 184~186°C (prepared in ethanol).

Found: N, 17.65. Calcd. for $C_{16}H_{23}N_5O_8$: N, 16.94%.

3,6-Dimethyltetrahydro-1,8-naphthylidine (XXVII).—By pyrolysis of crude XXV (0.71 g.) at 330°C a crystalline substance (carbonate of XXVII ?) was deposited on the neck of the reaction flask. This crystalline product was acidified with hydrochloric acid and treated with excess sodium hydroxide to liberate the free base, which was then extracted with benzene to give XXVII in the form of colorless plates; m. p., 110~111°C (from benzene-petroleum ether); yield, 0.02 g.

Found: C, 74.33; H, 8.65; N, 17.41. Calcd. for $C_{10}H_{14}N_2$: C, 74.03; H, 8.63; N, 17.26%.

The Monopicrate of XXVII.—M. p., 256°C (decomp.) (prepared in benzene). Found: C, 49.42; H, 4.49; N, 17.93. Calcd. for $C_{16}H_{17}N_5O_7$: C, 49.16; H, 4.38; N, 17.90%.

Dehydrogenation of XXVII.—In an atmosphere of nitrogen, compound XXVII (0.11 g., in 2 ml. of diphenyl ether) was heated at 250~280°C for 20 hr. in the presence of a palladium catalyst (0.2 g.). The reaction mixture was treated by a method similar to that described for XX in order to obtain the dehydrogenated product (0.05 g.); m. p., 191~192°C (from benzene), undepressed on admixture with the specimen of XX.

Hydrogenation of XXVII.—By a method similar to that described for XVII, compound XXVII (0.2 g., in 130 ml. of amyl alcohol) was treated with sodium (7 g.). A hydrogenated product (0.2 g.) was obtained; m. p., 162~163°C (from benzene), undepressed on admixture with the specimen of XVII.

3-(ω-Amino-*n*-propyl)-piperidone-2 (XXVIII).—By a method similar to that described for XXV, potassium salt of XXIV (28 g.) was hydrogenated in the presence of a Raney-nickel catalyst (prepared from 25 g. of Ni-Al alloy 50 : 50), giving crude XXVIII (13 g.).

The Picrate of XXVIII.—M. p., 207°C* (prepared in ethanol). Found: N, 18.11. Calcd. for $C_{14}H_{19}N_5O_8$: N, 18.18%.

Hexahydro-1,8-naphthylidine (XXX).—By a method similar to that described for XXVII, crude XXX was obtained from XXVIII in the form of a basic sticky substance which gave the picrate.

The Monopicrate of XXX.—M. p., 228~230°C (decomp.) (prepared in benzene). Found: C, 46.59; H, 4.00; N, 18.94. Calcd. for $C_{14}H_{15}N_5O_7$: C, 46.03; H, 4.14; N, 17.91%.

The author is grateful to Mr. Masatomo Kusunose (manager of Research Institute, Toho Rayon Co., Ltd.), Mr. Masahiko Takikawa (chief of the Laboratory to which the author belongs), Dr. Masakazu Taniyama (Toho Beslon Co., Ltd.), Dr. Torakichi Yoshioka (Profossor of Tokushima Univ.), Dr. Hisaya Tani (Professor of Osaka Univ.), Dr. Minoru Imoto (Professor of Osaka City Univ.) and Dr. Eizi Ochiai (ITSUU Lab., Tokyo) for their valuable advice on his experiments; to Mr. Takumi Okauchi, Mr. Yukihide Furutsu and Mr. Hiroshi Saijo for their help; to Mr. Toshikazu Inoue, Miss Keiko Yano and Miss Akiko Hiroshe, who helped him with the elementary analysis, and to Mr. Yoshiyuki Nishiyama and Mr. Kiyosumi Kubo, who helped him with the infrared spectra work.

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12) K. Nakanishi, "Sekigai Kyūshū Supekutoru" (Infrared Absorption Spectra), Nankōdō, Tokyo (1960), p. 51.

* This melting point agrees with that reported by Reissert[8].