

this sirup to dissolve it and then to yield a fine amorphous precipitate. This was collected by filtration, thoroughly washed with ether, dried in a vacuum desiccator and crystallized from hot methanol to give 0.2 g. (2.3% based on *N*-acetyl-tetra-*O*-acetyl-*D*-glucosamine) as colorless needles; decomposing point 324–326° (after gradual charring),  $[\alpha]_D^{20} +2.5^\circ$  (*c* 0.2, chloroform).

*Anal.* Calcd. for  $C_{28}H_{40}N_2O_{17}$ : C, 49.70; H, 5.96; N, 4.14. Found: C, 49.58; H, 6.03; N, 4.23.

IIIc is soluble in hot water, hot methanol, chloroform and acetone and insoluble in ether and petroleum ether. It did not reduce Fehling solution under ordinary conditions, but after heating in 3 *N* hydrochloric acid for 5 hr., it reduced Fehling solution.

Attempted experiments to prepare 1-(*D*-glucosaminido)-

*D*-glucose acetate (1-*O*-(2-acetamido-2-deoxy- $\beta$ -*D*-glucosyl)-*D*-glucoside heptaacetate) by shaking the chloroform solution of acetobromoglucosamine from 10 g. of *N*-acetyl-tetra-*O*-acetyl-*D*-glucosamine with 10 g. of silver oxide, 0.5 g. of iodine, 5 g. of 2,3,4,6-tetra-*O*-acetyl-*D*-glucose<sup>25</sup> and 20 g. of anhydrous sodium sulfate resulted in the isolation of IIIc.

**Acknowledgment.**—The authors gratefully acknowledge the generous supply of *D*-glucosamine hydrochloride by Kaken-Yaku Kako Co., Ltd., Yamashina, Kyoto.

(25) C. M. McCloskey and G. H. Coleman, *Org. Syntheses*, **25**, 53 (1944)

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## Heterocyclic Compounds. IV. The Structures of 2-Phenylpyrroline and 2,4-Diphenylpyrroline

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Chemical and spectral evidence is presented for ascribing the  $\Delta^1$ -structure to the 2,4-diphenylpyrroline obtained by reductive cyclization of 1,3-diphenyl-4-nitro-1-butanone and to the 2-phenylpyrroline obtained from the reaction of phenylmagnesium bromide with  $\gamma$ -chlorobutyronitrile.

The exact assignment of the position of unsaturation in pyrrolines has been the subject of repeated misinterpretation and contradiction. Much of the difficulty stems from the arbitrary assignment of a  $\Delta^2$ -pyrroline structure (such as II) to the examples of these compounds reported in the earlier literature.<sup>2–5</sup> In at least one instance<sup>6</sup> such a structure was assigned to a compound which proved later not to be a pyrroline at all.<sup>7</sup>

It is conceivable that some of these earlier investigators silently entertained the opinion to which Sonn<sup>8</sup> eventually gave expression; that is, that  $\Delta^1$ - and  $\Delta^2$ -pyrrolines are chemically indistinguishable.

However, the application of both physical and chemical methods recently has provided evidence that many pyrrolines, such as myosmine<sup>9</sup> and those obtained from reactions of Grignard reagents with  $\gamma$ -chlorobutyronitrile<sup>10–12</sup> or from reduction of certain pyrroles,<sup>12</sup> are best represented by  $\Delta^1$ -structures. Indeed, Witkop<sup>9</sup> has come to the conclusion that "there are probably no authentic secondary  $\Delta^2$ -pyrrolines."

Evidence now is presented for ascribing the  $\Delta^1$ -

structure to the 2,4-diphenylpyrroline obtained by reductive cyclization of 1,3-diphenyl-4-nitro-1-butanone (I), and to the 2-phenylpyrroline prepared for parallel study by the reaction of phenylmagnesium bromide with  $\gamma$ -chlorobutyronitrile.

Kohler and Drake<sup>13</sup> reported that hydrogenation of 1,3-diphenyl-4-nitro-1-butanone (I) over platinum black gave disappointing results which depended on factors that could not be controlled. Reduction was not confined to a single step and gave only oily products. 2,4-Diphenylpyrroline was not reported to be among the reduction products.<sup>14</sup> However, by reducing the nitro ketone with acetic acid and zinc or iron, Sonn<sup>8</sup> was able to obtain a 42% yield of 2,4-diphenylpyrroline.

We now have found that low pressure hydrogenation of 1,3-diphenyl-4-nitro-1-butanone (I) over ordinary Raney nickel at 25° affords a 79% yield of 2,4-diphenylpyrroline. With freshly prepared Raney nickel the reaction proceeds further to give a 77% yield of 2,4-diphenylpyrrolidine. One may reasonably assume that stepwise reduction occurs.

(13) E. P. Kohler and N. L. Drake, *ibid.*, **45**, 2144 (1923).

(14) Kohler and Drake obtained a solid, m.p. 179–180°, by treatment of their mixture of reduction products with benzoyl chloride. They ascribed to this derivative the composition  $C_{22}H_{19}NO_2$  and cited its formation as evidence that the reduction mixture contained an hydroxylated diphenylpyrroline. However, it is not unlikely that this benzoyl derivative is identical with 4-benzoylamino-1,3-diphenyl-1-butanone (VIII),  $C_{22}H_{21}NO_2$ , m.p. 180–181°, obtained by Sonn<sup>8</sup> from the reaction of benzoyl chloride with "2,4-diphenyl- $\Delta^2$ -pyrroline" (II), and by us (with m.p. 182–183°) similarly from 2,4-diphenyl- $\Delta^1$ -pyrroline (IV). Thus, the benzoyl derivative obtained by Kohler and Drake may have resulted from the presence of 2,4-diphenylpyrroline, rather than an hydroxylated pyrroline, in their mixture of reduction products.

It is likely, moreover, that the benzoyl derivative, m.p. 180° obtained by Rupe and Cisiger<sup>5</sup> from "2,4-diphenyl- $\Delta^1$ -pyrroline" also is the aforementioned amido ketone. On the basis of an analysis for nitrogen, these authors ascribed to their derivative the structure 1-benzoyl-2,4-diphenylpyrroline. However, this analysis is an inadequate criterion since the cyclic and acyclic amides in question do not differ sufficiently in nitrogen content.

(1) Partially abstracted from a portion of the Ph.D. dissertation of Jack L. Pinkus. Previous papers in this series include M. C. Kloetzel, J. E. Little and D. M. Frisch, *J. Org. Chem.*, **18**, 1511 (1953), and I. J. Pachter and M. C. Kloetzel, *THIS JOURNAL*, **74**, 971 (1952).

(2) R. Hielscher, *Ber.*, **31**, 277 (1898).

(3) S. Gabriel and J. Colman, *ibid.*, **41**, 513 (1908).

(4) S. Gabriel, *ibid.*, **42**, 1238 (1909).

(5) H. Rupe and F. Cisiger, *Helv. Chim. Acta*, **8**, 338 (1925).

(6) A. Wohl, *Ber.*, **34**, 1914 (1901).

(7) F. E. King, J. R. Marshall and P. Smith, *J. Chem. Soc.*, 239 (1951).

(8) A. Sonn, *Ber.*, **68**, 148 (1935).

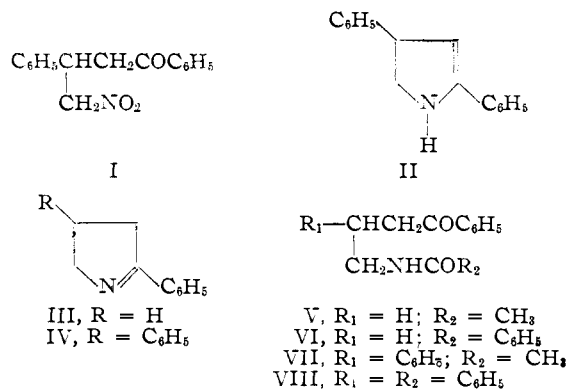
(9) B. Witkop, *THIS JOURNAL*, **76**, 5597 (1954).

(10) J. B. Cloke, *ibid.*, **51**, 1174 (1929); P. Lipp and H. Seeles, *Ber.*, **62**, 2456 (1929); J. B. Cloke, L. H. Baer, J. M. Robbins and C. E. Smith, *ibid.*, **67**, 2155 (1945).

(11) P. M. Maginnity with J. B. Cloke, *ibid.*, **73**, 49 (1951).

(12) G. C. Evans, *ibid.*, **73**, 5230 (1951).

for the pure pyrroline also is hydrogenated smoothly to the pyrrolidine in the presence of fresh catalyst. None of the pyrrolidine results from disproportionation of the pyrroline<sup>15</sup> for the latter is not affected even by extended treatment at 42° with fresh Raney nickel in ethanol.<sup>16</sup>



The same 2,4-diphenylpyrroline is obtained, in yields up to 43 and 39%, respectively, when the nitro ketone I is reduced by hydrazine in the presence of Raney nickel or by zinc dust and aqueous ammonium chloride. In the latter instance, part of the product is isolated as a complex with zinc chloride unless all ionic zinc is first precipitated as the sulfide. The catalyzed hydrazine reduction of aromatic nitro compounds has been reported previously,<sup>18,19</sup> but the method does not appear to have been applied to aliphatic nitro compounds heretofore.<sup>20</sup>

The 2,4-diphenylpyrroline obtained from these reductions was characterized by formation of several solid salts and evidently is identical with that obtained by Rupe and Gisiger<sup>5</sup> and by Sonn.<sup>8</sup> There is no band in the NH region in its infrared absorption spectrum, although the general level of absorption at 2.5–3.5  $\mu$  is relatively high (Nujol mull). Moreover, changes in the infrared spectrum accompanying protonation of the basic nitrogen parallel those described by Witkop for the spectra of myosmine (2- $\beta$ -pyridyl- $\Delta^1$ -pyrroline)<sup>9</sup> and other Schiff bases.<sup>22</sup> For example, the spectrum of 2,4-diphenylpyrroline hydrochloride shows a broad ammonium band at 3.80–4.08  $\mu$  with a maximum at 3.91  $\mu$  (compare 3.94  $\mu$  for myosmine monohydrochloride); immonium absorption occurs at 5.34  $\mu$  (at 5.30  $\mu$  for myosmine monohydrochloride); and the hypsochromic shift of the conjugated C=N band from 6.19  $\mu$  in the spectrum of the free base to 6.05  $\mu$  in the spectrum of the hydrochloride also is observed. These spectral characteristics are in harmony with the  $\Delta^1$ -structure (IV) for this 2,4-diphenylpyrroline.

(15) Compare J. P. Wibaut and J. Th. Hackmann, *Rec. trav. chim.*, **51**, 1157 (1932).

(16) Rogers<sup>17</sup> has reported that prolonged heating of 2,4-diphenylpyrroline at 350° produced only a trace of the corresponding pyrrole.

(17) M. A. T. Rogers, *J. Chem. Soc.*, 590 (1943).

(18) L. P. Kuhn, *THIS JOURNAL*, **73**, 1510 (1951).

(19) D. Balcom and A. Furst, *ibid.*, **75**, 4334 (1953).

(20) Chubb<sup>21</sup> first employed this method for reduction of  $\gamma$ -nitro ketones in this Laboratory in 1952.

(21) F. L. Chubb, Doctoral Dissertation, University of Southern California, 1952.

(22) B. Witkop, *Experientia*, **10**, 420 (1954).

Zerewitinoff determinations at 25° and at 100° provided confirmatory evidence for the structure of 2,4-diphenyl- $\Delta^1$ -pyrroline (IV). Neither significant active hydrogen nor addition of methylmagnesium iodide was detected and the base was recovered in greater than 90% yield. Inertness of the azomethine group toward addition of Grignard reagent is to be expected, since the unsaturated carbon bears no hydrogen, but the compound might be expected to react through its enamine form.<sup>23</sup> The fact that no reaction occurs may be taken as evidence that 2,4-diphenyl- $\Delta^1$ -pyrroline is not readily tautomerized.

Acetylation and benzylation of 2,4-diphenyl- $\Delta^1$ -pyrroline (IV) occur with concurrent rupture of the heterocyclic ring to yield acyclic amido ketones VII and VIII, respectively. As in the case of the benzylation product,<sup>14</sup> amido ketone VII was erroneously assigned a cyclic structure (1-acetyl-2,4-diphenyl- $\Delta^2$ -pyrroline) by Rupe and Gisiger<sup>5</sup> on the basis of inadequate evidence. Their analysis for nitrogen failed to disclose the presence of the second oxygen atom in this compound, whose structure we have ascertained by means of analytical and infrared absorption data.

Dehydrogenation of 2,4-diphenyl- $\Delta^1$ -pyrroline (IV) was effected readily with sulfur or selenium, to produce 2,4-diphenylpyrrole in yields of 69 or 49%, respectively. Rogers<sup>17</sup> has obtained a 55% yield with selenium under similar conditions but reported that the use of sulfur gave inferior yields.

2-Phenylpyrroline, prepared by the method of Craig, Bulbrook and Hixon,<sup>24</sup> displayed spectral and chemical properties similar to those of 2,4-diphenyl- $\Delta^1$ -pyrroline. No unequivocal conclusion could be drawn from an examination of the 3  $\mu$  region in the infrared absorption spectrum of the free base.<sup>25</sup> However, conversion to the hydrochloride resulted in the appearance of broad ammonium absorption with a maximum at 3.88  $\mu$ , immonium absorption at 5.33  $\mu$ , and the hypsochromic shift of the conjugated C=N band from 6.18  $\mu$  (in the base) to 6.06  $\mu$  in the infrared spectrum.

Consistent with a  $\Delta^1$ -structure (III) for this pyrroline was the fact that a Zerewitinoff determination in anisole detected neither the presence of active hydrogen nor addition of methylmagnesium iodide.<sup>26</sup>

(23) M. S. Kharash and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 1208.

(24) L. C. Craig, H. Bulbrook and R. M. Hixon, *THIS JOURNAL*, **53**, 1831 (1931).

(25) In our experience, the NH region in the infrared absorption spectra of pyrrolidines and pyrrolines is difficult to interpret. Intensity of absorption in this region varies considerably, depending both upon the nature of substituents in the vicinity of the nitrogen atom and upon the medium in which the spectrum is determined.

(26) Maginnity and Cloke<sup>11</sup> reported that 2-phenylpyrroline caused no gas evolution upon contact with methylmagnesium iodide for 30 hours but "consumed" 1 mole of Grignard reagent. These authors referred to the product of this reaction as an "addition complex" and stated that "analysis of the reaction mixture demonstrated that a considerable portion of the original compound was recovered unchanged." Evidently the complex was decomposed by water and no addition of Grignard reagent to azomethine linkage had occurred. Under these circumstances it is difficult to understand how the complex could resist hydrolysis, during decomposition of excess Grignard reagent with water in the customary Zerewitinoff procedure, and so lead to the conclusion that Grignard reagent had been "consumed."

2-Phenyl- $\Delta^1$ -pyrroline (III) was characterized through its solid hydrochloride, picrate and methiodide. As in the case of its 2,4-diphenyl analog, acetylation and benzoylation of this base occur with simultaneous ring cleavage. The structures of the resulting amides (V and VI, respectively) have been confirmed spectroscopically.

**Acknowledgment.**—The authors are indebted to Parke, Davis and Co., Detroit, Mich., for generous financial aid which made this study possible, and to R. Bruce Scott, Research Department, Parke, Davis and Co., for his help in determining and interpreting infrared spectra during the initial stages of this investigation.

### Experimental<sup>27</sup>

**2,4-Diphenyl- $\Delta^1$ -pyrroline.**—Catalytic hydrogenation of 1,3-diphenyl-4-nitro-1-butanone (I) was effected at room temperature by shaking a slurry of the ketone<sup>28</sup> (20 g.) and Raney nickel<sup>29</sup> (4 g.) in ethanol (200 ml.) for 28.5 hours under hydrogen at a pressure of 38–48 p.s.i. Distillation of the filtered solution yielded 13 g. (79%) of 2,4-diphenyl- $\Delta^1$ -pyrroline (IV), b.p. 154–155° at 2 mm., which solidified in the receiver; m.p. 50–52°. Crystallization from ether furnished colorless needles, m.p. 52°; Sonn<sup>8</sup> reported a m.p. of 48–49°. Rupe and Gisiger<sup>5</sup> evidently obtained the same compound, m.p. 50°, by reduction of 2,4-diphenyl-4-oxobutanonitrile but designated it 2,4-diphenyl- $\Delta^2$ -pyrroline (II).

*Anal.* Calcd. for  $C_{16}H_{15}N$ : C, 86.84; H, 6.83; N, 6.33; mol. wt., 221. Found: C, 86.83; H, 6.82; N, 6.29; mol. wt., 225 (Rast method, in exaltone).

The infrared absorption spectrum determined on a Nujol mull of this base showed principal maxima at 6.19, 6.36, 6.71, 7.45, 9.26, 9.52, 9.80, 13.12 (broad) and 14.27  $\mu$  (broad).

The base decolorized a 3% solution of bromine in carbon tetrachloride but not a 1% solution of potassium permanganate in acetone.

2,4-Diphenyl- $\Delta^1$ -pyrroline in anhydrous ether reacted with anhydrous hydrogen chloride to produce the insoluble hydrochloride, which subsequently crystallized from benzene in colorless, hygroscopic needles, m.p. 165–166.5° with slight decomposition (sealed tube).

*Anal.* Calcd. for  $C_{16}H_{15}ClN$ : C, 74.55; H, 6.25; N, 5.43. Found: C, 74.56; H, 6.36; N, 5.60.

The infrared absorption spectrum of the hydrochloride, determined on a Nujol mull, showed principal maxima at 3.91 (broad), 5.34, 6.05, 6.16, 6.25, 6.33, 6.68, 7.47, 7.76, 8.38, 9.75, 10.84 (broad) and 13.32  $\mu$  (broad).

2,4-Diphenyl- $\Delta^1$ -pyrroline perchlorate, prepared in a mixture of isopropyl alcohol and ether and crystallized twice from a similar mixture containing some ethyl acetate, melted at 110.5–111.5°.

*Anal.* Calcd. for  $C_{16}H_{15}ClNO_4$ : Cl, 11.02. Found: Cl, 10.73.

The picrate formed readily in ethanol and separated from a mixture of chloroform and ether in green-yellow needles, m.p. 160–161° with sintering beginning at 157°. Rupe and Gisiger<sup>5</sup> and Sonn<sup>8</sup> reported 156° and 155–156°, respectively, for their picrates.

*Anal.* Calcd. for  $C_{22}H_{19}N_4O_7$ : C, 58.66; H, 4.03; N, 12.44. Found: C, 58.38; H, 4.32; N, 12.66.

The oxalate was prepared by adding a saturated acetone solution of anhydrous oxalic acid to an acetone solution of 2,4-diphenyl- $\Delta^1$ -pyrroline until no further precipitation occurred. After three crystallizations from ethyl acetate the colorless crystals sintered at 160° and melted at 168° with gas evolution. Rupe and Gisiger<sup>5</sup> reported 157–158°.

(27) Microanalyses are by William Schenck and Joseph Pirie, both formerly of the University of Southern California, and by Dr. Adalbert Elek, Elek Microanalytical Laboratories, Los Angeles, Calif. Infrared spectra were obtained with a Perkin-Elmer model 13 double beam spectrophotometer with sodium chloride prism and cells. Melting points are uncorrected.

(28) M. C. Kloetzel, *This Journal*, **69**, 2271 (1947).

(29) R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

*Anal.* Calcd. for  $C_{18}H_{17}NO_4$ : C, 69.44; H, 5.50; N, 4.50. Found: C, 69.19; H, 5.31; N, 4.40.

Zerewitinoff determinations on 2,4-diphenyl- $\Delta^1$ -pyrroline were conducted in anisole in the usual manner<sup>11,30</sup> and unused methylmagnesium iodide was back titrated by addition of water. At 25° the base evolved no methane and added no Grignard reagent. After completion of the determination, solid ammonium chloride and water were added to the reaction vessel and the contents were extracted with chloroform. Evaporation of the dried extract and addition of picric acid in ethanol yielded 90.4% of 2,4-diphenyl- $\Delta^1$ -pyrroline picrate which did not depress the m.p. of authentic picrate.

At 100°, 2,4-diphenyl- $\Delta^1$ -pyrroline likewise added no methylmagnesium iodide and evolved 0.09 mole of methane.

Acetylation of 2,4-diphenyl- $\Delta^1$ -pyrroline (822 mg.) was accomplished by heating for 2.5 hours at 100° with acetic anhydride (1 ml.). Addition of water (5 ml.) to the cooled mixture precipitated the product which rapidly crystallized; yield 882 mg. (84%), m.p. 91–101°. Recrystallization from ethyl acetate or a mixture of chloroform and ether afforded 4-acetylamino-1,3-diphenyl-1-butanone (VII) in colorless platelets (624 mg.), m.p. 100–104°. A final crystallization raised the m.p. to 105°, the m.p. of Rupe and Gisiger's product.<sup>5</sup>

The infrared absorption spectrum determined on a Nujol mull of VII showed principal maxima at 3.06  $\mu$  (N—H), 5.95  $\mu$  (ketone C=O), 6.08  $\mu$  (amido C=O) and 6.47–6.50  $\mu$  (amide).

*Anal.* Calcd. for  $C_{18}H_{19}NO_2$ : C, 76.84; H, 6.81; N, 4.98. Found: C, 76.55; H, 7.11; N, 4.69.

Benzoylation of 2,4-diphenyl- $\Delta^1$ -pyrroline (616 mg.) was accomplished by shaking with benzoyl chloride (1 ml.) and 10% aqueous sodium hydroxide (10 ml.) until excess benzoyl chloride was hydrolyzed. Crystallization of the crude product from ethyl acetate yielded 673 mg. (70%) of 4-benzoylamino-1,3-diphenyl-1-butanone (VIII) in colorless needles, m.p. 180–182°. The m.p. was raised to 182–183° by further crystallization.

A Nujol mull of VIII displayed infrared absorption maxima at 3.06  $\mu$  (N—H), 5.97  $\mu$  (ketone C=O), 6.12  $\mu$  (amido C=O) and 6.58  $\mu$  (amide).

*Anal.* Calcd. for  $C_{22}H_{21}NO_2$ : C, 80.44; H, 6.16; N, 4.08. Found: C, 80.42; H, 6.14; N, 4.11.

Dehydrogenation of 2,4-diphenyl- $\Delta^1$ -pyrroline (IV) was accomplished by heating 2.0 g. of the base with 2.2 g. of selenium at 250° for 3 hours in a slow stream of nitrogen. From a benzene extract of the cooled product 980 mg. (49%) of 2,4-diphenylpyrrole was obtained, m.p. 175–178°. Recrystallization from ethanol yielded colorless microcrystals, m.p. 178–179°, the m.p. reported by Rogers.<sup>17</sup>

When a mixture of 440 mg. of IV and 64 mg. of sulfur was heated, evolution of hydrogen sulfide began at 180°. The temperature was then raised to 260° over a period of 7 minutes. A decolorized toluene solution of the reaction product yielded 2,4-diphenylpyrrole in colorless needles, m.p. 176–178°, yield 300 mg. (69%).

Hydrogenation of 2,4-diphenyl- $\Delta^1$ -pyrroline (2.21 g.) in ethanol (20 ml.) was effected in 5 hours at 25° and 45 p.s.i. in the presence of 1 g. of freshly prepared Raney nickel. The oily product (1.92 g.) distilled at 150–155° at 1 mm. pressure and was treated with 1.8 ml. of phenyl isothiocyanate in the usual manner. The resulting phenylthiourea (2.06 g.) formed colorless plates, m.p. 188–189°, which did not depress the m.p. of the phenylthiourea prepared from authentic 2,4-diphenylpyrrolidine.<sup>28</sup>

When 15 g. of 1,3-diphenyl-4-nitro-1-butanone (I) in 150 ml. of anhydrous ethyl acetate was hydrogenated for 26 hours under similar conditions in the presence of 5 g. of freshly prepared Raney nickel, 2,4-diphenylpyrrolidine was again the product; yield 9.5 g. (77%), b.p. 155° at 1 mm. pressure. A liquid film of this base showed an infrared absorption maximum at 2.96  $\mu$ ; in chloroform solution, at 2.98  $\mu$ . The phenylthiourea melted at 189–190° and did not depress the m.p. of a sample prepared from authentic 2,4-diphenylpyrrolidine.

A solution of 2,4-diphenyl- $\Delta^1$ -pyrroline (368 mg.) in absolute ethanol (10 ml.) was stirred with Raney nickel (1 g.) for 17.5 hours at 42°. Unchanged pyrroline (81%) was

(30) S. Siggia, "Quantitative Organic Analysis, Via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 44.

recovered as the picrate, m.p. 159–160°, and the residual oily material, after being washed with aqueous sodium hydroxide to remove excess picric acid, gave no phenylthiourea when treated with phenyl isothiocyanate.

**Reduction of 1,3-Diphenyl-4-nitro-1-butanone (I) with Hydrazine and Raney Nickel.**—During a period of 3 hours, a solution of 8 ml. of 85% hydrazine hydrate in 12 ml. of methanol was added to a mechanically stirred mixture of 10 g. of the nitro ketone I, 100 ml. of methanol and 2 g. of Raney nickel (4 months old) maintained at 35–40°. Stirring was continued for 3 hours after all nitro ketone had dissolved and the catalyst was then removed by filtration. Evaporation of the filtrate yielded an oil (from which a small amount of solid was filtered) which distilled at 150–158° at 12–13 mm. to give 3.53 g. (43%) of 2,4-diphenyl- $\Delta^1$ -pyrroline (IV), m.p. 47–50°. Recrystallized material did not depress the m.p. of the pyrroline obtained from the aforementioned hydrogenation of nitro ketone I.

**Reduction of 1,3-Diphenyl-4-nitro-1-butanone (I) with Zinc and Aqueous Ammonium Chloride.**—To a mechanically stirred mixture of 20 g. of nitro ketone I, 24 g. of ammonium chloride, 80 ml. of water and 330 ml. of methanol, maintained at a temperature of 10–15°, were added 4-g. portions of 90% zinc dust every 15 minutes until a total of 96 g. had been added. Stirring and cooling were prolonged for an additional period of 2 hours and the solids were then removed by filtration and washed with methanol. The combined filtrates were concentrated to a volume of 75 ml. under reduced pressure and the aqueous layer was decanted.

The residual oil partially solidified and was extracted with 50 ml. of ethyl acetate. The colorless insoluble solid (5.88 g.) melted at 202–212°; recrystallization from ethanol gave small needles, m.p. 227°.

*Anal.* Calcd. for  $(C_{16}H_{15}N)_2ZnCl_2$ : C, 66.39; H, 5.22; N, 4.84. Found: C, 66.30; H, 5.31; N, 4.35.

Distillation of the ethyl acetate solution yielded 5.25 g. (32%) of 2,4-diphenyl- $\Delta^1$ -pyrroline (IV), b.p. 162–165° at 3 mm., m.p. 45–47°. Recrystallized material did not depress the m.p. of the pyrroline obtained from hydrogenation of nitro ketone I.

In another instance, all zinc was removed from the filtered aqueous methanol reduction solution by precipitation with hydrogen sulfide. The filtered solution was then concentrated and extracted with ether continuously for at least 36 hours. Benzene was added to the ether extract to redissolve some oil which had separated. Distillation of the dried solution under reduced pressure then yielded 6.5 g. (39%) of 2,4-diphenyl- $\Delta^1$ -pyrroline.

**2-Phenyl- $\Delta^1$ -pyrroline.**—A sample of the base prepared by the method of Craig, Bulbrook and Hixon<sup>24</sup> distilled at 88–89° at 3 mm. and then separated from petroleum ether (b.p. 30–35°) in large colorless plates, m.p. 41–42°. Gabriel and Colman<sup>3</sup> reported 44–45°.

*Anal.* Calcd. for  $C_{10}H_{11}N$ : C, 82.71; H, 7.64; N, 9.65. Found: C, 82.53; H, 7.59; N, 9.61.

The infrared absorption spectrum determined on a liquid film of the base showed principal maxima at 3.22, 3.36, 6.18, 6.34, 6.68, 6.90, 7.47, 9.54, 9.72, 10.10, 10.34, 10.85, 13.10 (broad) and 14.37  $\mu$  (broad).

The base decolorized bromine in carbon tetrachloride solution but not 2% potassium permanganate in acetone.

The hydrochloride was crystallized from a mixture of ethyl acetate and ether; m.p. 210.5–212.5° with sintering from 205°. Gabriel and Colman<sup>3</sup> reported 210–212° with sintering from 200°.

*Anal.* Calcd. for  $C_{10}H_{12}ClN$ : C, 66.12; H, 6.66; N, 7.71. Found: C, 65.57; H, 6.53; N, 8.14.

The hydrochloride showed infrared absorption maxima

(Nujol mull) at 3.88 (broad), 5.33, 6.06, 6.25, 7.51, 7.60, 8.41, 8.67, 9.46, 10.16, 10.69 (broad) and 13.19  $\mu$  (broad).

The picrate of 2-phenyl- $\Delta^1$ -pyrroline separated from ethanol in glistening plates, m.p. 196.5–198.5° dec. Gabriel and Colman reported 198° and Sonn<sup>8</sup> 198° dec.

**2-Phenyl- $\Delta^1$ -pyrroline Methiodide.**—A mixture of 0.58 g. of the base, 5 ml. of 12% sodium hydroxide in aqueous methanol (2.5:1) and 1.0 g. of dimethyl sulfate was stirred at 62° for 1.5 hours and then allowed to stand at 25° for 12 hours. After being twice extracted with ether, the aqueous phase of the reaction mixture was made slightly acidic with hydrochloric acid. Dropwise addition of concentrated aqueous sodium iodide afforded colorless platelets of the methiodide in 44% yield, m.p. 221–224°. Recrystallization from ethanol raised the m.p. to 237–238°.

*Anal.* Calcd. for  $C_{11}H_{14}IN$ : C, 46.01; H, 4.91; N, 4.88; I, 44.20. Found: C, 45.71; H, 5.02; N, 4.59; I, 44.05.

**Behavior of 2-Phenyl- $\Delta^1$ -pyrroline toward Methylmagnesium Iodide.**—A Zerewitinoff determination in anisole at 29° showed 0.02 mole of active hydrogen and 0.01 mole of Grignard reagent addition. Unchanged pyrroline was recovered in 93.4% yield in the manner previously described for the 2,4-diphenyl analog.

An attempt was made to force a reaction between 2-phenyl- $\Delta^1$ -pyrroline and Grignard reagent in the following manner. Over a period of 45 minutes, a solution of 2.0 g. of the base in 25 ml. of anisole was added to the Grignard reagent prepared from 3.1 ml. of methyl iodide, 1.16 g. of magnesium and 25 ml. of anisole. The mixture was heated on a steam-bath during addition of the base and then for an additional period of 2.5 hours. Stirring was continued at 25° for 2.2 hours and then the mixture was decomposed with aqueous ammonium chloride. After removal of anisole the residual oil yielded 4.408 g. (85.4%) of the picrate of 2-phenyl- $\Delta^1$ -pyrroline which did not depress the m.p. of an authentic sample.

A slurry of the picrate in ether was shaken with 10% aqueous lithium hydroxide. The ether layer yielded 75.5% of 2-phenyl- $\Delta^1$ -pyrroline which did not depress the m.p. of an authentic sample and whose infrared absorption spectrum was identical with that of an authentic sample.

**Acetylation of 2-phenyl- $\Delta^1$ -pyrroline,** as described for the 2,4-diphenyl analog, produced 4-acetylamino-1-phenyl-1-butanone (V) in 73% yield, m.p. 89–93.5°. Recrystallization from aqueous ethanol or from ethyl acetate furnished colorless platelets, m.p. 94–95°.

*Anal.* Calcd. for  $C_{12}H_{15}NO_2$ : C, 70.22; H, 7.36; N, 6.82. Found: C, 70.04; H, 7.27; N, 6.54.

The infrared absorption spectrum determined on a Nujol mull of V showed principal maxima at 3.00  $\mu$  (N—H), 5.97  $\mu$  (ketone C=O), 6.07  $\mu$  and 6.12  $\mu$  (amido C=O), 6.26  $\mu$  (phenyl) and 6.41–6.46  $\mu$  (amide).

**Benzoylation of 2-phenyl- $\Delta^1$ -pyrroline,** as described for the 2,4-diphenyl analog, yielded 64% of crude product, m.p. 120–123°. Recrystallization from acetone or ethanol gave pure 4-benzoylamino-1-phenyl-1-butanone (VI) in colorless platelets, m.p. 124.5–125.5°. Gabriel and Colman<sup>3</sup> and Sonn<sup>8</sup> obtained benzoyl derivatives melting at 125–126 and 126°, respectively.

*Anal.* Calcd. for  $C_{17}H_{17}NO_2$ : C, 76.38; H, 6.41; N, 5.24. Found: C, 76.51; H, 6.23; N, 5.04.

A Nujol mull of VI displayed infrared absorption maxima at 3.05  $\mu$  (N—H), 5.97  $\mu$  (ketone C=O), 6.13  $\mu$  (amido C=O), 6.27  $\mu$ , 6.37  $\mu$ , and 6.45, 6.48 and 6.52  $\mu$  (amide triplet) and 6.73  $\mu$ ; in chloroform solution at 2.93–2.99  $\mu$  (N—H), 5.95  $\mu$  (ketone C=O), 6.02  $\mu$  (amido C=O), 6.27  $\mu$ , 6.34  $\mu$  and 6.74  $\mu$ .

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