

The reaction mixture was stirred for an additional 5 min. and allowed to stand for 12 hr., after which time it was diluted with cold water. The resulting precipitate, after drying and crystallization from benzene-petroleum ether, weighed 13.4 g. (52%); m.p. 95°.

*Anal.* Calcd. for  $C_{14}H_{14}N_2O_3$ : C, 65.00; H, 5.43. Found: C, 65.09; H, 5.42.

**Ethyl 6-Methoxy-8-quinolylmalonamate.**—This compound was prepared by the same procedure used to prepare ethyl 8-quinolylmalonamate. From 20 g. (0.12 mole) of 6-methoxy-8-aminoquinoline and 17.5 g. (0.12 mole) of carbethoxyacetyl chloride there was obtained 21.2 g. of crude material. An analytical sample, crystallized from benzene-petroleum ether, melted at 113–114°.

*Anal.* Calcd. for  $C_{15}H_{16}N_2O_4$ : C, 62.50; H, 5.55. Found: C, 62.52; H, 5.60.

**8-Quinolylmalonic Acid.**—A solution of 10 g. (0.039 mole) of ethyl 8-quinolylmalonamate and 20 g. of sodium bicarbonate in 270 ml. of water and 30 ml. of ethanol was heated for 4 hr. on a steam bath with vigorous stirring. The solution was cooled and acidified to pH 5 with hydrochloric acid. The precipitated product was removed by filtration and dried; yield, 7 g. An analytical sample, crystallized from water and a little alcohol, melted at 138–139° dec.

*Anal.* Calcd. for  $C_{12}H_{10}N_2O_3$ : C, 62.60; H, 4.35. Found: C, 62.64; H, 4.19.

**6-Methoxy-8-quinolylmalonic Acid.**—A suspension of 5.6 g. (0.02 mole) of ethyl 6-methoxy-8-quinolylmalonamate

in 60 ml. of water containing 6.3 g. of dissolved sodium bicarbonate was heated with stirring on a steam bath for 3 hr. Water was added occasionally to maintain the original volume. After treatment of the hot solution with Darco and filtration, solid sodium chloride was added to the cooled solution, which was then acidified to pH 2. The precipitated crude product was removed by filtration and crystallized from water; yield, 4.9 g. (96.8%), m.p. 145° dec.

*Anal.* Calcd. for  $C_{13}H_{12}N_2O_4$ : C, 59.99; H, 4.65. Found: C, 60.01; H, 4.85.

**2,4-Dihydroxy-1,10-phenanthroline.**—A mixture of 1.6 g. (0.007 mole) of 8-quinolylmalonic acid and 50 g. of polyphosphoric acid was heated in an oil bath at 130° for 2 hr. with occasional stirring. The reaction mixture was diluted with cold water and neutralized with concentrated aqueous ammonia. The resulting product was removed by filtration and dried; yield, 1.1 g. An analytical sample, crystallized from aqueous acetic acid, melted at 315–316° with prior sintering.

*Anal.* Calcd. for  $C_{12}H_8N_2O_2$ : C, 67.92; H, 3.80; N, 13.20. Found: C, 68.17; H, 4.20; N, 13.00.

**2,4-Dihydroxy-5-methoxy-1,10-phenanthroline.**—From 5 g. (0.02 mole) of 6-methoxy-8-quinolylmalonic acid and 75 g. of polyphosphoric acid, treated as above, there was obtained 4.6 g. of dry, crude product. An analytical sample melted at 250–251° after crystallization from ethanol.

*Anal.* Calcd. for  $C_{13}H_{10}N_2O_3$ : C, 64.46; H, 4.16. Found: C, 64.76; H, 4.36.

## Angularly Arylated Decahydroquinolines, Hexahydroindolines, and Octahydropyridine

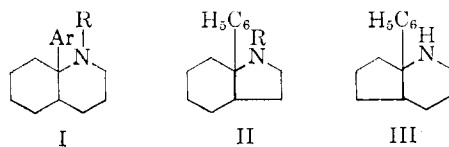
ERIK F. GODEFROI<sup>1</sup> AND LYDIA H. SIMANYI

Research Laboratories of Parke, Davis & Co., Ann Arbor, Michigan

Received March 23, 1962

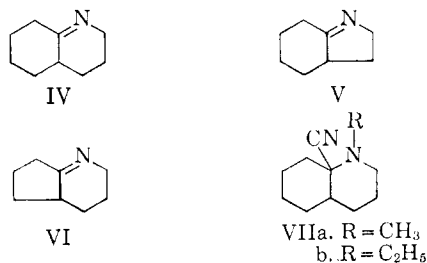
The addition of aryllithium reagents to cyclic Schiff's bases IV, V, and VI has given decahydro-8a-arylquinolines (I), hexahydro-7a-phenylindolines (II), and octahydro-7a-phenyl-1H-1-pyridine (III). N-Alkylated derivatives of I have also been obtained by treating N-substituted carbonitriles (VIIa and VIIb) with Grignard reagents. The products have been found to possess central nervous system depressant properties.

During the course of investigations on substances possessing central nervous system depressant properties, we prepared a number of decahydro-8a-arylquinolines (I), hexahydro-7a-phenylindolines (II), and octahydro-7a-phenyl-1H-1-pyridine (III).



Examination of the literature revealed that decahydro-4a-phenylquinoline, isomeric with type I, had been previously prepared by Boekelheide<sup>2a</sup> and Sugimoto,<sup>2b</sup> but their methods were not applicable to the preparation of the desired compounds.

The addition of organolithium reagents to anils<sup>3</sup> suggested that the reaction of aryllithium reagents to cyclic imines IV, V, and VI would produce types I, II, and III respectively.



2,3,4a,5,6,7,8-Octahydroquinoline (IV) was prepared according to directions of Cohen and Witkop<sup>4</sup> and Parcell.<sup>5</sup> This imine reacted with a number of aryllithium reagents to yield decahydro-

(1) Present address: Research Laboratories, Dr. C. Janssen, Beerse, Belgium.

(2)(a) V. Boekelheide, *J. Am. Chem. Soc.*, **69**, 790 (1947). (b) N. Sugimoto, H. Kugita, and T. Fijita, *J. Pharm. Soc. Japan*, **75**, 177 (1955).

(3) H. Gilman and R. H. Kirby, *J. Am. Chem. Soc.*, **55**, 1265 (1933); *ibid.*, **63**, 2046 (1951).

(4) L. A. Cohen and B. Witkop, *J. Am. Chem. Soc.* **75**, 6595 (1955).

(5) R. F. Parcell, *ibid.*, **81**, 2596 (1959).

TABLE I  
 DECAHYDRO-8A-ARYLQUINOLINES

Comp.	Ar	R	B.p.	HCl salt, m.p.	Method <sup>a</sup>	Emp. form.	Calcd.		Found	
							C	H	C	H
1	C <sub>6</sub> H <sub>5</sub>	H	115-117°/ 0.09 mm.	285-286°	A	C <sub>15</sub> H <sub>21</sub> N	83.66	9.83	83.35	9.82
2	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	115-117°/ 0.12 mm.	209-210°	B) C)	C <sub>16</sub> H <sub>23</sub> N·HCl	72.29	9.10	72.50	9.26
3	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	120-123°/ 0.12 mm.	207-208°	D	C <sub>17</sub> H <sub>25</sub> N·HCl	72.96	9.36	73.21	9.39
4	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>4</sub> OH	...	201-202°	E	C <sub>17</sub> H <sub>25</sub> NO·HCl	69.01	8.86	69.19	8.95
5	C <sub>6</sub> H <sub>5</sub>	(CH <sub>2</sub> ) <sub>2</sub> COOCH <sub>3</sub>	...	162-164°	F	C <sub>18</sub> H <sub>27</sub> NO <sub>2</sub> ·HCl	67.53	8.32	67.99	8.67
6	C <sub>6</sub> H <sub>5</sub>	(CH <sub>2</sub> ) <sub>3</sub> OH	...	185-187°	G	C <sub>18</sub> H <sub>27</sub> NO·HCl	69.85	9.11	69.87	8.87
7	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>	118-123°/ 0.11 mm.	...	D	C <sub>19</sub> H <sub>29</sub> NO	79.38	10.17	79.47	10.01
8	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>4</sub> SC <sub>2</sub> H <sub>5</sub>	130-135°/ 0.1 mm.	...	D	C <sub>19</sub> H <sub>29</sub> NS	75.19	9.60	75.55	9.31
9	<i>m</i> -Tolyl	H	117-120°/ 0.09 mm.	247-248°	A	C <sub>16</sub> H <sub>23</sub> N·HCl	72.29	9.10	72.13	9.20
10	<i>m</i> -Tolyl	CH <sub>3</sub>	111-117°/ 0.1 mm.	203-204°	C	C <sub>17</sub> H <sub>25</sub> N·HCl	72.96	9.36	72.41	9.44
11	<i>m</i> -Chloro-phenyl	H	...	252-240°	A	C <sub>16</sub> H <sub>20</sub> ClN·HCl	62.96	7.40	63.03	7.54
12	2-Thienyl	H	100-108°/ 0.1 mm.	270-271°	A	C <sub>13</sub> H <sub>13</sub> NS·HCl	60.56	7.82	60.32	7.98
13	2-Thienyl	CH <sub>3</sub>	108-116°/ 0.2 mm.	143-144°	B) C)	C <sub>14</sub> H <sub>21</sub> NS·HCl	61.84	8.16	61.84	8.09
14	2-Thienyl	C <sub>2</sub> H <sub>5</sub>	102-104°/ 0.09 mm.	...	B	C <sub>15</sub> H <sub>23</sub> NS	72.23	9.29	72.45	9.10
15	2-Furyl	CH <sub>3</sub>	61-72°/ 0.1 mm.	207-208°	B	C <sub>14</sub> H <sub>21</sub> NO·HCl	65.73	8.67	65.98	9.00
16	2-Furyl	C <sub>2</sub> H <sub>5</sub>	87-91°/ 0.2 mm.	190-191°	B	C <sub>15</sub> H <sub>23</sub> NO·HCl	66.77	8.97	66.67	9.01

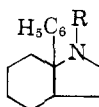
<sup>a</sup> (A) Addition of ArLi to IV. (B) Reaction of ArMgBr with type VII. (C) Clarke-Eschweiler methylation of compounds 1, 9, and 12. (D) Respective acylation and lithium aluminum hydride reduction of compound 1. (E) Treatment of 2 equivalents of compound 1 with 1 equivalent of ethyl bromoacetate in refluxing toluene followed by lithium aluminum hydride reduction of the ester. (F) Reaction of compound 1 with methyl acrylate in refluxing methanol for 18 hr. (G) Lithium aluminum reduction of compound 5.

8a-arylquinolines (I. R = H). It appears that this reaction is particularly sensitive to steric hindrance, for although phenyl-, *m*-tolyl-, and *m*-chlorophenyllithium reacted with IV in fair yields, the use of *o*-tolyllithium under identical conditions gave negligible amounts of the desired product. The secondary amines obtained by this method were subsequently converted to a number of N-alkyl derivatives by the following procedures. Treatment of type I (R = H) with formaldehyde and formic acid led to the N-methyl analogs. The higher N-alkyl derivatives were obtained by acylation of the secondary amines followed by reduction of the resulting amides with lithium aluminum hydride. Octahydro-8a-phenyl-1(2H)-quinolineethanol was prepared by the alkylation of decahydro-8a-phenylquinoline with ethyl bromoacetate, and subsequent lithium aluminum hydride reduction of the resulting amino acid ethyl ester. A similar reduction of the product obtained from I (Ar = phenyl; R = H) and methyl acrylate gave octahydro-8a-phenyl-1(2H)-quinoline-propanol.

Low yields attained by the addition of certain aryllithium reagents to IV prompted investigation of other routes leading to type I. The reaction of  $\alpha$ -aminocarbonitriles with Grignard reagents has been known to proceed with the displacement of the cyano group to give benzylicamines.<sup>6</sup> Although excessive bulkiness of amine substituents was found to affect this reaction adversely, it was hoped that participation of one of the nitrogen substituents into a bicyclic system would reduce the steric effects. Furthermore, this method would offer the additional advantage of providing common intermediates for I in which the aryl group could be varied while keeping substituent R constant.

Compound IV reacted with an excess of methyl iodide in acetonitrile to give the corresponding methiodide. The latter, upon treatment with sodium cyanide, yielded octahydro-1-methyl-8a-(1H)-quinolinecarbonitrile (VIIa). Phenylmagnesium bromide subsequently converted VIIa to N-methyldecahydro-8a-phenylquinoline. This

(6) H. M. Taylor and C. R. Hauser, *J. Am. Chem. Soc.*, **82**, 1960 (1960); (b) E. F. Godefroi, *D. Auslegeschrift*, 1, 111, 175 (1961).

TABLE II  
 HEXAHYDRO-7A-PHENYLINDOLINES


R	Base, b.p.	HCl salt, m.p.	Emp. form.	Calcd.		Found	
				C	H	C	H
H	95-98°/0.115 mm.	264-265°	C <sub>14</sub> H <sub>19</sub> N	83.53	9.51	82.27	9.82
-CH <sub>3</sub>	115-120°/0.120 mm.	...	C <sub>22</sub> H <sub>21</sub> N	83.66	9.83	83.8g	10.00
-C <sub>2</sub> H <sub>5</sub>	105-109°/0.110 mm.	...	C <sub>18</sub> H <sub>23</sub> N	83.79	10.11	83.55	10.41

product was in all respects identical to the compound obtained previously by adding phenyllithium to IV, followed by methylation of the secondary amine.

Octahydro-1-ethyl-8a(1H)-quinolinecarbonitrile (VIIb) was prepared in a fashion similar to the one described for VIIa. Both VIIa and VIIb, upon treatment with 2-thienylmagnesium bromide and 2-furylmagnesium bromide furnished the desired products of type I—*i.e.*, compounds 13-16.

A tabulation of the decahydro-8a-arylquinolines prepared has been presented in Table I.

Attention was focused next on the preparation of hexahydro-7a-phenylindolines (II). The Schiff's base 3,3a,4,5,6,7-hexahydro-2H-indole (V) required as intermediate for type II had been previously reported by a number of investigators.<sup>7</sup> In our hands it was prepared by an extension of the method described by Cohen and Witkop<sup>4</sup> for the preparation of IV. 1-(N-Pyrrolidino)-cyclohexene reacted with chloro- or iodoacetonitrile in methyl alcohol to give 2-oxocyclohexane acetonitrile in 20% yield. This nitrile was reconverted to the pyrrolidine enamine, reduced with lithium aluminum hydride and hydrolyzed to 2-(β-aminoethyl)-cyclohexanone which cyclized spontaneously to V. Addition of phenyllithium to this imine afforded hexahydro-7a-phenylindoline (II, R = H) in 31% yield. The N-methyl and N-ethyl homologs of this compound listed in Table II were prepared by methods described above for the preparation of the N-alkyl derivatives of the decahydro-8a-phenylquinolines.

Further extension of the Cohen-Witkop method<sup>4</sup> gave the hitherto unreported 3,4,4a,5,6,7-hexahydro-2H-1-pyridine (VI), representing the Schiff's base needed to prepare III. The low yield obtained by the addition of phenyllithium to VI was in sharp contrast to the yields attained in comparable additions to IV and V. However, the reluctance of the organolithium reagent to add to VI is not unexpected if one considers VI to constitute a nitrogen analog of cyclopentanone. The diminished ketonic character of cyclopentanones as compared with cyclohexanones is well known and is believed to be

founded in the greater increase in I-strain associated with carbonyl reactions of cyclopentanone.<sup>8</sup> There is no reason to assume that similar effects might not also be operative in the reactions of the Schiff's bases derived from five- and six-membered ketones.

**Pharmacology.**—Compounds of types I, II, and III have exhibited central nervous system depressant properties similar to the ones described by Chen *et al.*<sup>9</sup> Detailed pharmacological data will be reported at a later date.

### Experimental

The general procedure used for the addition of organolithium reagents to the cyclic Schiff's bases to give compounds 1, 9, 11, 12, and 17 is best exemplified by the preparation of compound 1.

**Decahydro-8a-phenylquinoline (Compound 1).**—To a solution of phenyllithium prepared from 141 g. (0.90 mole) of bromobenzene and 13.7 g. (1.95 g.-atoms) of lithium ribbon in 750 ml. of ether was added slowly and with stirring a solution of 58 g. (0.42 mole) of octahydroquinoline (IV) in 100 ml. of ether. The reaction which was slightly exothermic, was stirred at room temperature for 2 hr. The lithium adduct was then decomposed by the cautious addition of 250 ml. of water after which the ether phase was washed two more times with water. Drying of the ether solution over magnesium sulfate and stripping of the solvent left an oily residue. This material, upon distillation through a short Vigreux column gave, after an appreciable forerun of unchanged octahydroquinoline, 36 g. (40% yield) of product, boiling at 115-118° at 0.09 mm.

Anal. Calcd. for C<sub>15</sub>H<sub>21</sub>N: C, 83.66; H, 9.83; N, 6.51. Found: C, 83.55; H, 9.82; N, 6.72.

The amine formed a hydrochloride salt melting at 285-286° (methanol-ether). The N-acetyl derivative melted at 55-56°.

**N-Methyldecahydro-8a-phenylquinoline (Compound 2).**—To a mixture of 21.5 g. (0.10 mole) of decahydro-8a-phenylquinoline and 10.1 g. (0.22 mole) of formic acid was introduced 8.70 g. of 38% formaldehyde. The reaction was allowed to proceed on the steam bath with stirring for 3 hr. The solution was rendered alkaline by the addition of excess 5 N sodium hydroxide. Subsequent extraction of the free base with ether, followed by drying and removal of the solvent left the crude product. Infrared examination of this material exhibited no N-H bands. Distillation yielded 15.2 g. (66%) of product boiling at 115-117°/0.09 mm.

Anal. Calcd. for C<sub>16</sub>H<sub>23</sub>N: C, 83.79; H, 10.11. Found: C, 83.51; H, 10.24.

The addition of isopropanolic hydrochloric acid to an

(7) (a) F. E. King, *J. Chem. Soc.*, **260** (1953). (b) B. Belleau, *J. Am. Chem. Soc.*, **75**, 5765 (1953). (c) B. Witkop, *ibid.*, **78**, 2873 (1956). (d) B. Belleau, *Can. J. Chem.*, **35**, 651 (1957).

(8) (a) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Am. Chem. Soc.*, **73**, 212 (1951). (b) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

(9) G. Chen, C. R. Ensor, D. Russell, and B. Bohner, *J. Pharmacol. Exptl. Therap.*, **127**, [3], 241 (1959).

etheral solution of the base afforded upon recrystallization from isopropyl alcohol-ether an amine hydrochloride hydrate, m.p. 100–105°. An anhydrous salt was obtained after two recrystallizations from dioxane-ether and melted at 209–210° (platelets).

**N-Ethyldecahydro-8a-phenylquinoline Hydrochloride (Compound 3).**—A solution of 6.19 g. (0.240 mole) of N-acetyldecahydro-8a-phenylquinoline in 50 ml. of ether was added in a stream to a stirred solution of 3.0 g. of lithium aluminum hydride in 300 ml. of ether. The mixture was stirred for 5 hr. and was then decomposed by the respective additions of 3 ml. of water, 2.25 ml. of 5 N sodium hydroxide, and 10.5 ml. of water. After removal of the inorganic solids by filtration and the addition of isopropanolic hydrochloric acid to the filtrate, there was obtained 5.2 g. of amine hydrochloride. A hydrated form (m.p. ca. 110°) was obtained upon recrystallization from methanol-ether; recrystallization from benzene raised the melting point to 207–208°.

*Anal.* Calcd. for  $C_{17}H_{23}N \cdot HCl$ : C, 72.96; H, 9.36. Found: C, 72.21; H, 9.39.

**Octahydro-1-methyl-8a(1H)-quinolinecarbonitrile (VIIa).** A solution of 137 g. (1.0 mole) of IV and 81 ml. (1.30 moles) of methyl iodide in 800 ml. of acetonitrile was refluxed for 1 hr. Removal of the solvent *in vacuo* left an oil which was induced to crystallize by the addition of 500 ml. of ether. The methiodide was removed by filtration and was not purified further. It was slightly hygroscopic.

The quaternary salt was dissolved in 250 ml. of glacial acetic acid and to it was added dropwise and with stirring at 10° a solution of 54 g. (1.10 moles) of sodium cyanide in 80 ml. of water. Upon allowing the reaction to proceed for 5 hr. at room temperature, the solution was poured into 1000 ml. of ice water. Treatment with base of the resulting solution, followed by extraction with ether, drying of the organic phase, and stripping of the solvent, left an oil. This residue upon fractionation through a Vigreux column yielded 82 g. (46% yield) of pure product boiling at 115–118°/8 mm.

The nitrile solidified on standing to a crystalline mass. An analytical sample prepared by recrystallization from petroleum ether melted at 38–40°.

*Anal.* Calcd. for  $C_{11}H_{13}N_2$ : C, 74.10; H, 10.17. Found: C, 74.01, 10.25.

**N-Methyl-8a(2-thienyl)decahydroquinoline (Compound 13).**—To a stirred solution of 2-thienylmagnesium bromide in 200 ml. of ether [prepared from 30 g. (0.185 mole) of 2-bromothiophene and 6.2 g. (0.26 mole) of magnesium] was added dropwise a solution of 21 g. (0.12 mole) of VIIa in 50 ml. of ether. The mixture was then stirred for an additional 3.5 hr. and was decomposed by the introduction of 250 ml. of saturated ammonium chloride solution. After separation of the phases the organic layer was washed with fresh water, dried, and stripped of solvent. Vacuum distillation of the oily residue gave, after a considerable forerun boiling at 7;–75°/0.250 mm., 10 g. of product, a yellow sirup, b.p. 108–116°/0.250 mm. This represents a 36% yield.

The free base in ether was converted to the hydrochloride salt by the addition of isopropanolic hydrogen chloride. Recrystallization of this material from methyl alcohol-ether afforded the product melting at 143–144°. Further recrystallization from isopropyl alcohol did not raise the melting point.

*Anal.* Calcd. for  $C_{14}H_{21}NS \cdot HCl$ : C, 61.84; H, 8.17. Found: C, 61.84; H, 8.09.

**Octahydro-1-ethyl-8a(1H)-quinolinecarbonitrile (VIIb).**—This material, b.p. 120–125°/9 mm., was prepared by the reaction of IV and ethyl iodide in acetonitrile, followed by treatment of the resulting ethiodide quaternary salt with sodium cyanide in aqueous acetic acid, in the fashion described for the preparation of VIIa.

**N-Ethyl-8a-(2-furyl)decahydroquinoline (Compound 16).**—To a stirred solution of butyllithium prepared from 52 ml.

(0.48 mole) of butyl bromide and 6.9 g. (1.0 g.-atom) of lithium ribbon in 500 ml. of ether was added 24 ml. (0.33 mole) of furan in 15 ml. of ether. To the resulting 2-furyllithium, which was stirred an additional 0.5 hr., was added anhydrous magnesium bromide in ether, prepared from 62 g. (0.33 mole) of ethylene dibromide and 8.2 g. of magnesium in 150 ml. of ether. The resulting 2-furylmagnesium bromide<sup>10</sup> was stirred for another half hour when 34 g. (0.18 mole) of VIIb in 50 ml. of ether was introduced dropwise. The reaction was then allowed to proceed overnight. The Grignard complex was decomposed by the addition of 500 ml. of saturated ammonium chloride solution. The organic phase upon washing, drying, and removal of ether, gave the crude product. Final purification was achieved by vacuum distillation and gave 34 g. (81% yield) of pure product b.p. 87–89°/0.20 mm.

The hydrochloride salt, prepared by the addition of isopropanolic hydrogen chloride to ethereal free base, and recrystallized from methyl alcohol-ether, melted at 179–181°.

*Anal.* Calcd. for  $C_{16}H_{23}N \cdot OHCl$ : C, 66.77; H, 8.91. Found: C, 66.67; H, 9.01.

**3,3a,4,5,6,7-Hexahydro-2H-indole (V).**—This compound, b.p. 68–73°/14 mm. was prepared in 25% over-all yield from 2-oxycyclohexanecarbonitrile in a fashion similar to the one described for the preparation of IV.<sup>4</sup> The procedure used for the preparation of the starting material is presented in detail.

**2-Oxycyclohexanecarbonitrile—1-(N-Pyrrolidino)cyclohexene,** 930 g. (6.15 moles), 620 g. (8.27 moles) of chloroacetonitrile, and 1500 ml. of methyl alcohol were refluxed for 18 hr. The solvent was then taken off in vacuum and to the residue there was added 200 ml. of water. The aqueous phase was subsequently extracted three times with ether, after which the organic layer in turn was washed, first with dilute hydrochloric acid, then with 5% sodium bicarbonate solution, and again with water. Drying of the ether phase followed by evaporation of the solvent afforded a residual oil which upon distillation gave 170 g. of product oiling at 100–102°/0.20 mm. This represents a 20% yield.

*Anal.* Calcd. for  $C_8H_{11}NO$ : N, 10.21; Found: N, 10.31.

The ketonitrile, upon reaction with pyrrolidine, gave the enamine, boiling at 110–112°/0.20 mm. in 81% yield.

**3,4,4a,5,6,7-Hexahydro-2H-pyridine (VI).**—The hydrolytic ring closure of 185 g. (0.95 mole) of 1-[2-(3-amino-propyl)-1-cyclopentenyl]pyrrolidine, which was in turn prepared by the lithium aluminum hydride reduction of 1-[2-(cyanoethyl)-1-cyclopentenyl]pyrrolidine<sup>11</sup> yielded VI, b.p. 68–70°/11 mm. in 73% yield. The material was converted to a picrate salt melting at 146–147°.

*Anal.* Calcd. for  $C_8H_{13}N \cdot C_6H_2(NO_2)_3OH$ : N, 15.91. Found: N, 15.98.

**Octahydro-7a-phenyl-1H-1-pyridine (III).**—The reaction of ca. 1.0 mole of phenyllithium with 85 g. (0.69 mole) of VI, according to the method given for compound 1, gave, after a large forerun consisting mostly of VI, 11 g. (8% yield) of product, b.p. 87–95°/0.10 mm. The hydrochloride salt, upon recrystallization from water, melted at 237–238°.

*Anal.* Calcd. for  $C_{14}H_{19}N \cdot HCl$ : C, 70.75; H, 8.48. Found: C, 70.99; H, 8.58.

**Acknowledgment.**—Microanalytical results have been furnished by Mr. C. E. Childs and associates, and spectral data were supplied and interpreted by Messrs. R. B. Scott and E. Schoeb. The many helpful suggestions given by Dr. R. F. Parcell are herewith gratefully acknowledged.

(10) R. F. Parcell, U. S. Patent 2,921,076 (1960).

(11) G. Stork and H. K. Landesman, *J. Am. Chem. Soc.*, **78**, 5128 (1956).