

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Preparation of Some  $\beta$ -Aryl- $\beta$ -carboxypiperidonesBY RICHARD K. HILL, CHARLES E. GLASSICK<sup>1</sup> AND LEONARD J. FLIEDNER<sup>1</sup>

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Several 2-piperidones substituted at  $\beta$ -positions by aryl and carboxyl groups have been prepared by hydrogenation of appropriate Michael adducts. One of these, 5-phenyl-6-keto-nipecotic acid, was cyclized by polyphosphoric acid to a bridged tricyclic analog of the alkaloid cytisine. Attempts to use ethoxymethylene malonic ester derivatives as Michael components in routes to these compounds led instead to naphthalene and quinolizone derivatives.

During a study of synthetic routes to phenyl analogs of some of the lupin alkaloids, we have had occasion to prepare a number of 2-piperidones substituted at the  $\beta$ -positions with aryl (usually phenyl) and carboxyl groups. Since these bear a close relationship to the important group of analgesics represented by meperidine<sup>2</sup> (I), their synthesis is described in this communication. While the 3,3-disubstituted analog (II) prepared by Bergel and co-workers<sup>3</sup> is reported<sup>4</sup> to possess half the analgesic activity of meperidine, comparatively few other piperidines and piperidones with these  $\beta$ -substituents are known.

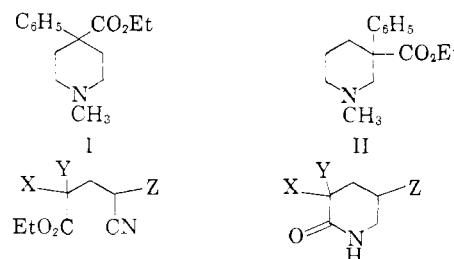
The general method employed in this synthesis is one developed mainly by Koelsch<sup>5</sup> and extended by others,<sup>6</sup> and consists of reductive cyclization of a cyanoester prepared by Michael addition. The substitution desired in the piperidones in this work necessitated  $\gamma$ -cyanoesters (III) substituted at the 2- and 4-positions as intermediates. These were prepared in the following manner.

Cyanoethylation of diethyl phenylmalonate yielded diethyl (2-cyanoethyl)-phenylmalonate<sup>7</sup> (IIIa), which was catalytically hydrogenated to ethyl 2-keto-3-phenylnipecotate (IVa). Hydrolysis and decarboxylation led to 3-phenyl-2-piperidone (IVb).

Addition of diethyl malonate to atroponitrile gave a 90% yield of ethyl  $\alpha$ -carbethoxy- $\gamma$ -cyano- $\gamma$ -phenylbutyrate (IIIb), whose structure was confirmed by hydrolysis to the known  $\gamma$ -cyano- $\gamma$ -phenylbutyric acid. Reduction of the cyanoester yielded ethyl 2-keto-5-phenylnipecotate (IVc). Although two stereoisomers are theoretically possible from this reaction, a high yield of one sharp-melting compound was obtained. Its configuration cannot be assigned with certainty, although the acid IVd obtained by alkaline hydrolysis almost surely has the more stable *cis* diequatorial conformation. Decarboxylation of this acid provided the known 5-phenyl-2-piperidone (IVe).

To reverse the positions of the substituents in the lactam IVd, ethyl cyanoacetate was added to

ethyl atropate, yielding diethyl  $\alpha$ -cyano- $\gamma$ -phenylglutarate (IIIc). Some difficulty was experienced initially in this addition by the subsequent ethoxide-catalyzed cleavage of one of the carbethoxyl groups, leading to IIId as the main product.<sup>8</sup> The cleavage of one carbethoxyl group from a



- IIIa, X = C<sub>6</sub>H<sub>5</sub>, Y = CO<sub>2</sub>Et, Z = H  
 b, X = H, Y = CO<sub>2</sub>Et, Z = C<sub>6</sub>H<sub>5</sub>  
 c, X = C<sub>6</sub>H<sub>5</sub>, Y = H, Z = CO<sub>2</sub>Et  
 d, X = C<sub>6</sub>H<sub>5</sub>, Y = H, Z = H  
 e, X = 2-pyridyl, Y = Z = H

- IVa, X = C<sub>6</sub>H<sub>5</sub>, Y = CO<sub>2</sub>Et, Z = H  
 b, X = C<sub>6</sub>H<sub>5</sub>, Y = H, Z = H  
 c, X = H, Y = CO<sub>2</sub>Et, Z = C<sub>6</sub>H<sub>5</sub>  
 d, X = H, Y = CO<sub>2</sub>H, Z = C<sub>6</sub>H<sub>5</sub>  
 e, X = H, Y = H, Z = C<sub>6</sub>H<sub>5</sub>  
 f, X = C<sub>6</sub>H<sub>5</sub>, Y = H, Z = CO<sub>2</sub>Et  
 g, X = C<sub>6</sub>H<sub>5</sub>, Y = H, Z = CO<sub>2</sub>H  
 h, X = 2-pyridyl, Y = Z = H

malonic ester is a well-recognized phenomenon,<sup>9</sup> and has been avoided by conducting the addition in an alcohol-free medium.<sup>10</sup> We found that another simple expedient was to use a fourfold excess of ethyl cyanoacetate, and by this procedure a nearly quantitative yield of adduct IIIc could be obtained. Catalytic reduction gave ethyl-6-keto-5-phenylnipecotate (IVf), which was hydrolyzed to the corresponding acid IVg. Again, the *cis* configuration seems more likely for the stereoisomer obtained.

Hydrogenation of the cyanoethylation product of ethyl 2-pyridylacetate (IIIe) over platinum in hydrochloric acid has been reported by Boekelheide, *et al.*,<sup>11</sup> to lead to a mixture of 3-(2-piperidyl)-piperidone-2 and 1-carbethoxyquinolizidine. We found that by carrying out the reduction in ethanol with Raney nickel, a high yield of the pyridyl-piperidone IVh was obtained.

Several attempts were made to utilize ethoxymethylene malonic ester derivatives as Michael

(1) Taken from the Ph.D. thesis of Charles E. Glassick, Princeton University, 1956, and from the senior thesis of Leonard J. Fliedner, Princeton University, 1958.

(2) C. M. Suter, in "Medicinal Chemistry," Vol. II, edited by F. F. Blicke and C. M. Suter, John Wiley and Sons, Inc., New York, 1956, p. 218.

(3) (a) F. Bergel, N. C. Hindley, A. L. Morrison and H. Rinderknecht, *J. Chem. Soc.*, 269 (1944); (b) F. Bergel, A. L. Morrison and H. Rinderknecht, U. S. Patent 2,446,803 (C. A., **43**, 695 (1949)).

(4) A. D. Macdonald, G. Woolfe, F. Bergel, A. L. Morrison and H. Rinderknecht, *Brit. J. Pharmacol. Chemotherapy*, **1**, 4 (1946).

(5) C. F. Koelsch, (a) *THIS JOURNAL*, **65**, 437 (1943); (b) **65**, 2093 (1943); (c) **65**, 2458 (1943); (d) **65**, 2459 (1943).

(6) W. Barr and J. W. Cook, *J. Chem. Soc.*, 438 (1945).

(7) M. F. Ansell and D. H. Hey, *ibid.*, 1863 (1950).

(8) Compound IIId was not isolated, but its presence was shown by hydrogenation of the total neutral product to a mixture containing predominantly 3-phenyl-2-piperidone.

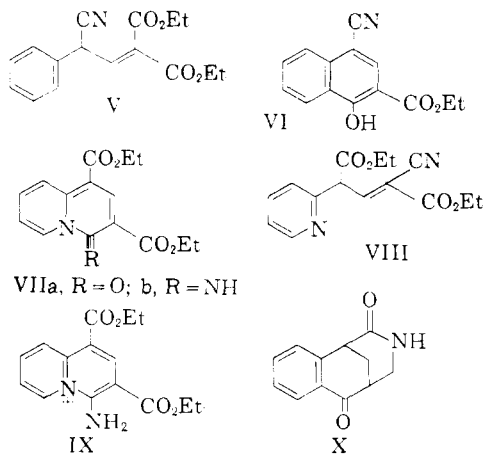
(9) (a) A. C. Cope and S. M. McElvain, *THIS JOURNAL*, **54**, 4319 (1932); (b) R. Connor, *ibid.*, **55**, 4597 (1933).

(10) V. Boekelheide and S. Rothchild, *ibid.*, **71**, 879 (1949).

(11) V. Boekelheide, W. J. Linn, P. O'Grady and M. Lamborg, *ibid.*, **75**, 3243 (1953).

components to obtain compounds such as V, which might also be hydrogenated to  $\beta$ -substituted piperidones. From the reaction of phenylacetonitrile and diethyl ethoxymethylenemalonate was isolated only a solid compound,  $C_{14}H_{11}NO_3$ , which was assigned the structure 2-carbethoxy-4-cyano-1-naphthol (VI) on the basis of its solubility in dilute base, a positive ferric chloride test and the presence of cyano and salicylate bands in the infrared spectrum. Compound VI is clearly formed by further base-catalyzed cyclization of V; similar reactions have been reported by Menon.<sup>12</sup>

The addition of ethyl 2-pyridylacetate to diethyl ethoxymethylenemalonate at 180° was discovered by Boekelheide and Lodge<sup>13</sup> to lead to the quinoline VIIa. In an attempt to isolate the presumed type of intermediate, such as compound VIII, which might be hydrogenated to a pyridylpiperidone, we carried out a lower temperature addition of pyridylacetic ester to ethyl ethoxymethylenecyanoacetate. The only product isolated was an orange solid to which the structure VIIb was assigned, on the basis of the data: (i) the empirical formula  $C_{15}H_{15}N_2O_4$ , (ii) solubility in dilute acid although VIIa is insoluble in this medium, (iii) the infrared spectrum which revealed a sharp N-H peak along with the disappearance of the nitrile function, and (iv) the ultraviolet spectrum which was similar to that of VIIa though shifted about 15–20 m $\mu$  toward the visible and with an added band in the visible. The spectrum was shifted appreciably in acid, consonant with the presence of such resonance structures for the salt as IX; such "aromatic" structures also account for the marked resistance of the imino group of VIIb toward acid hydrolysis.



Finally, it was of considerable interest to join the carboxyl and phenyl groups of piperidones IVd and IVg to produce bridged tricyclic systems analogous to that present in cytosine. Attempted cyclodehydration of IVd with hydrofluoric acid and polyphosphoric acid, even under mild conditions, led only to decarboxylation with the formation of 5-phenyl-2-piperidone, a result not too surprising in view of the lactam carbonyl beta to the carboxyl

in IVd. Piperidone IVg, however, was readily converted to compound X by hot polyphosphoric acid.

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### Experimental

Melting points were taken by capillary, and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer model 21 spectrophotometer, in chloroform or carbon tetrachloride solution.

**Ethyl 2-Keto-3-phenylnipecotate (IVa).**—Diethyl (2-cyanoethyl)-phenylmalonate (20 g.), prepared by the method of Ansell and Hey,<sup>7</sup> was hydrogenated in 125 ml. of glacial acetic acid in a Parr shaker at 60 pounds pressure over platinum dioxide until the theoretical amount of hydrogen had been absorbed. The catalyst was removed by filtration, and the filtrate diluted with 300 ml. of water, then neutralized with dilute sodium hydroxide solution and extracted with three 75-ml. portions of ether. The dried extracts were concentrated, and the residual oil refluxed in toluene for two hours. Evaporation of the solvent left a colorless solid which, recrystallized from aqueous ethanol, gave a 70% yield of ethyl 2-keto-3-phenylnipecotate, m.p. 142–143°. The infrared spectrum showed strong bands at 5.81 and 5.98  $\mu$ , corresponding to the ester and lactam functions.

*Anal.* Calcd. for  $C_{14}H_{17}NO_3$ : C, 67.99; H, 6.93; N, 5.66. Found: C, 68.02; H, 6.89; N, 5.62.

**3-Phenyl-2-piperidone (IVb).**—The residual oil remaining from the hydrogenation of 5 g. of diethyl (2-cyanoethyl)-phenylmalonate as described above was allowed to stand overnight with an ethanolic solution of 0.87 g. of potassium hydroxide. Hydrochloric acid (12.5 ml.) was added and the ethanol removed under reduced pressure. The residue was refluxed in xylene for two hours, the xylene distilled, and the residue recrystallized from ethanol. A colorless solid (1.0 g., 35% over-all) resulted which, after sublimation at 145° (0.5 mm.) and recrystallization from acetone, melted at 170–170.5°. Its infrared spectrum displayed a strong band at 5.99  $\mu$ , characteristic of the lactam group.

*Anal.* Calcd. for  $C_{11}H_{13}NO$ : C, 75.40; H, 7.48; N, 7.99. Found: C, 75.36; H, 7.50; N, 7.90.

**Ethyl  $\alpha$ -Carbethoxy- $\gamma$ -cyano- $\gamma$ -phenylbutyrate (IIIb).**—A solution of 5 g. of sodium and 80 g. of diethyl malonate in 250 ml. of absolute ethanol was cooled in an ice-bath while 50 g. of atropine<sup>14</sup> was added dropwise with stirring. After standing at room temperature for six days, the ethanol was distilled and the residue shaken with dilute hydrochloric acid, then extracted with ether. Fractionation of the dried ethereal solution gave 101 g. (90%) of ester distilling at 110–114° (0.01 mm.).

*Anal.* Calcd. for  $C_{16}H_{19}NO_4$ : C, 66.42; H, 6.62; N, 4.84. Found: C, 66.32; H, 6.61; N, 5.01.

**$\gamma$ -Cyano- $\gamma$ -phenylbutyric Acid.**—Ethyl  $\alpha$ -carbethoxy- $\gamma$ -cyano- $\gamma$ -phenylbutyrate (1.0 g.) was dissolved in 100 ml. of diethylene glycol containing 0.5 g. of potassium hydroxide, and kept at 50° for 24 hours. The solution was poured into 150 ml. of 0.05 N hydrochloric acid and extracted with chloroform. The extracts were dried over magnesium sulfate, concentrated, and heated to 190° in an oil-bath to ensure decarboxylation. The solid residue was recrystallized from ethanol, yielding 0.48 g. (73%) of the cyano-acid, m.p. 60.5–61° (lit.<sup>15</sup> m.p. 61°).

**Ethyl 2-Keto-5-phenylnipecotate (IVc).**—The reduction of 50 g. (0.17 mole) of ethyl  $\alpha$ -carbethoxy- $\gamma$ -cyano- $\gamma$ -phenylbutyrate in 150 ml. of glacial acetic acid was effected by Raney nickel in a Parr shaker at 60 lb. pressure. After the theoretical amount of hydrogen was taken up, the catalyst was filtered and the filtrate concentrated under reduced pressure. The residual oil was refluxed in ethyl alcohol for four hours, and yielded, after removal of the alcohol, 30.3 g. (75%) of colorless solid. Recrystallized from

(12) B. K. Menon, *J. Chem. Soc.*, 1061 (1935); 1775 (1936).

(13) V. Boekelheide and J. P. Lodge, Jr., *THIS JOURNAL*, **73**, 3681 (1951).

(14) J. F. Walker, U. S. Patent 2,478,990; *C. A.*, **44**, 2009 (1950).

(15) S. Wideqvist, *Svensk Kem. Tid.*, **54**, 34 (1942); *C. A.*, **37**, 5046 (1943).

ethanol, it melted at 108.5–109.5°; the infrared spectrum showed strong bands at 5.76 and 6.00  $\mu$ .

*Anal.* Calcd. for  $C_{19}H_{17}NO_3$ : C, 67.99; H, 6.93; N, 5.65. Found: C, 67.85; H, 6.96; N, 5.66.

**2-Keto-5-phenylnipecotic Acid (IVd).**—Hydrolysis of the ester was accomplished by allowing 2.4 g. of ethyl 2-keto-5-phenylnipecotatate in 100 ml. of absolute ethanol containing 0.56 g. of potassium hydroxide to stand at room temperature for two days. The solution was treated with 150 ml. of dilute aqueous potassium hydroxide, filtered, and the filtrate acidified in the cold. The acid was extracted with chloroform, dried over magnesium sulfate, and obtained by evaporation at reduced pressure. The yield was 1.5 g. (71.5%) of colorless solid, which could be recrystallized by slow evaporation of an acetone solution. The acid melted at 104–105° with evolution of gas; the melt resolidified and on continued heating remelted at 125–127°.

*Anal.* Calcd. for  $C_{12}H_{13}NO_3$ : C, 65.74; H, 5.98. Found: C, 65.82; H, 6.03.

**5-Phenyl-2-piperidone (IVe).**—2-Keto-5-phenylnipecotic acid (1.5 g.) was heated at 115° for 30 minutes and the resulting brown solid sublimed at 100° *in vacuo*. The colorless sublimate weighed 0.98 g. (81%) and melted at 125–125.8° (lit.<sup>5b</sup> m.p. 127–129°). The infrared spectrum had a strong band at 5.99  $\mu$ .

*Anal.* Calcd. for  $C_{11}H_{13}NO$ : C, 75.40; H, 7.48; N, 7.99. Found: C, 75.47; H, 7.38; N, 7.97.

**Diethyl  $\alpha$ -Cyano- $\gamma$ -phenylglutarate (IIIc).**—To 200 ml. of absolute ethanol was added, with cooling, 2.9 g. (0.128 mole) of sodium, 58 g. (0.512 mole) of ethyl cyanoacetate and 22.5 g. (0.128 mole) of ethyl atropate.<sup>16</sup> After standing at room temperature for three days, the alcohol was distilled and the residual oil taken up in ether and washed with dilute hydrochloric acid. The dried ethereal extracts were distilled through a short column, yielding 35.8 g. (97%) of colorless liquid, b.p. 130–135° (0.03 mm.). The yield was diminished markedly if an equimolar amount rather than a fourfold excess of ethyl cyanoacetate was used.

*Anal.* Calcd. for  $C_{16}H_{19}NO_4$ : C, 66.42; H, 6.62; N, 4.84. Found: C, 66.24; H, 6.50; N, 4.94.

**Ethyl 5-Phenyl-6-ketonipecotatate (IVf).**—Diethyl  $\alpha$ -cyano- $\gamma$ -phenylglutarate (14.4 g., 0.05 mole) was hydrogenated in 100 ml. of glacial acetic acid in a Parr shaker at 60 lb. pressure over Raney nickel catalyst. When the theoretical amount of hydrogen had been absorbed, the catalyst was filtered and the filtrate concentrated at reduced pressure. The residual oil was refluxed in benzene for 6 hours, washed with dilute aqueous bicarbonate, and the benzene evaporated. The residue crystallized on cooling its ether solution, yielding 11 g. (92%) of colorless solid, m.p. 118–119°. The infrared spectrum displayed strong bands at 5.78 and 6.0  $\mu$ .

*Anal.* Calcd. for  $C_{14}H_{17}NO_3$ : C, 67.99; H, 6.93; N, 5.66. Found: C, 67.79; H, 6.61; N, 5.95.

When equimolar quantities of ethyl atropate, ethyl cyanoacetate and sodium ethoxide were used in the Michael addition, and the resulting adduct carried through to hydrogenation without careful fractionation, the main product was 3-phenyl-2-piperidone, m.p. 170–171°, identified by its infrared spectrum, analysis and mixed melting point with the sample described above.

**5-Phenyl-6-ketonipecotic Acid (IVg).**—Ethyl 5-phenyl-6-ketonipecotatate (1.15 g.) was dissolved in 75 ml. of absolute ethanol containing 0.3 g. of potassium hydroxide and allowed to stand overnight at room temperature. The solvent was removed by distillation at reduced pressure, the residue taken up in water and acidified with dilute hydrochloric acid. The mixture was extracted with ethyl acetate, the extracts dried over magnesium sulfate and concentrated at reduced pressure. The residue was recrystallized from ethyl acetate, yielding 0.55 g. (54%) of colorless product, m.p. 194–195°.

*Anal.* Calcd. for  $C_{12}H_{13}NO_3$ : C, 65.74; H, 5.98; N, 6.39. Found: C, 65.99; H, 5.89; N, 6.47.

**7,8-Benz-2,6-diketo-3-azabicyclo(3,3,1)nonane (X).**—5-phenyl-6-ketonipecotic acid (0.45 g.) was stirred into 30 g. of polyphosphoric acid and heated at 100° for one hour. The warm solution was poured into a mixture of ice and water, stirred until homogeneous, neutralized with ammo-

nium hydroxide and extracted thoroughly with chloroform. The extracts were dried and evaporated, and the residue recrystallized from ether, yielding 0.28 g. (67%) of colorless solid, m.p. 201–202°.

*Anal.* Calcd. for  $C_{12}H_{11}NO_2$ : C, 71.62; H, 5.51; N, 6.96. Found: C, 71.37; H, 5.44; N, 6.89.

**The 2,4-dinitrophenylhydrazones** were difficult to purify, due to its insolubility. After digestion with 95% ethanol, it melted at 322–323°.

*Anal.* Calcd. for  $C_{18}H_{15}N_5O_5 \cdot \frac{1}{2}H_2O$ : C, 55.38; H, 4.13. Found: C, 55.12; H, 3.96.

**$\gamma$ -Carbethoxy- $\gamma$ -(2-pyridyl)-butyronitrile (IIIe).**—The method of Boekelheide, *et al.*,<sup>11</sup> was modified in the following manner. To a solution of 20 g. (0.12 mole), of ethyl 2-pyridylacetate in 75 ml. of anhydrous ether was added 0.1 g. of sodium, and the mixture refluxed until the sodium dissolved. A solution of acrylonitrile (3.2 g., 0.078 mole) in 20 ml. of ether was added and refluxing continued for 14 hours. After cooling, the solution was washed with 50 ml. of saturated ammonium chloride solution and dried over sodium sulfate. Distillation through a short column yielded 12 g. (75%) of yellow liquid, b.p. 130–150° (0.2 mm.), lit. b.p. 137–140° (0.7 mm.).

**3-(2-Pyridyl)-2-piperidone (IVh).**—A solution of 10 g. (0.485 mole) of IIIe in 100 ml. of absolute ethanol was hydrogenated in a Parr shaker over Raney nickel catalyst at 60 lb. pressure. When the theoretical amount of hydrogen had been taken up, the catalyst was removed by filtration and the filtrate refluxed for four hours, then concentrated. The residue, partially crystalline, was recrystallized from ethanol, yielding 2.2 g. of colorless solid. A second crop of 1.2 g. was obtained by refluxing the filtrate for an hour and cooling, bringing the yield to 85%. Recrystallized twice from ethanol, the lactam melted at 145–147.5° and showed a strong infrared band at 5.99  $\mu$ .

*Anal.* Calcd. for  $C_{10}H_{12}N_2O$ : C, 68.16; H, 6.86; N, 15.90. Found: C, 67.84; H, 6.71; N, 15.92.

**2-Carbethoxy-4-cyano-1-naphthol (VI).**—Phenylacetoneitrile (5.9 g., 0.05 mole) and diethyl ethoxymethylenemalonate (5.4 g., 0.025 mole) were added to a solution of 0.57 g. (0.025 g. atom) of sodium in 100 ml. of absolute ethanol and the mixture refluxed for two hours. The deep red solution was poured into 200 ml. of dilute hydrochloric acid and extracted with ether. Vacuum distillation of the dried extracts gave only solvent and some recovered phenylacetoneitrile, but recrystallization of the solid residue in the distilling flask from ethanol yielded 3.0 g. of colorless solid, m.p. 92.0–92.7°.

*Anal.* Calcd. for  $C_{14}H_{11}NO_3$ : C, 69.70; H, 4.59; N, 5.80. Found: C, 69.58; H, 4.51; N, 5.77.

The compound was soluble in dilute sodium hydroxide, gave a positive ferric chloride test, and showed strong bands in the infrared at 4.50  $\mu$  (nitrile) and 5.99  $\mu$  (salicylate<sup>17</sup>).

**1,3-Dicarbethoxy-4-quinolizimide (VIIb).**—To a solution of 5.0 g. (0.033 mole) of ethyl 2-pyridylacetate and a catalytic amount of sodium ethoxide in benzene was added 5.12 g. (0.033 mole) of ethyl- $\alpha$ -cyano- $\beta$ -ethoxyacrylate in 30 ml. of benzene. The solution was kept at 10° during the addition, then allowed to come to room temperature overnight. The red solution was extracted with 150 ml. of 0.6 *N* hydrochloric acid and the extracts neutralized with potassium carbonate, yielding 3.0 g. of orange solid. After vacuum sublimation and recrystallization from acetone, it melted at 128–129°, but when mixed with an authentic sample of 1,3-dicarbethoxy-4-quinolizone (VIIa), the melting point was depressed to 112–127°.

*Anal.* Calcd. for  $C_{15}H_{18}N_2O_4$ : C, 62.49; H, 5.59; N, 9.72. Found: C, 62.72; H, 5.52; N, 9.77.

This compound was recovered unchanged after standing overnight in 10% sulfuric acid at room temperature. It was also recovered largely unchanged from brief boiling with hydrochloric acid and sodium nitrite; ultraviolet absorption:  $\lambda_{max}$  (EtOH) 221 (23,200), 275 (16,600) sh., 282 (17,100), 360 (11,500) sh., 368 (12,300), 448 (10,700). In ethanolic hydrochloric acid, the maxima were shifted to 216 (27,500), 265 (14,000) sh., 271 (15,700), 338 (11,800) and 395 (16,100).

PRINCETON, N. J.

(17) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 157.

(16) H. Schinz and M. Hinder, *Helv. Chim. Acta*, **30**, 1349 (1947).