

as described for other compounds in this paper or (2) by stannous chloride reduction in hydrochloric acid followed by treatment with alkali (98.5% yield).<sup>7</sup>

To 3.6 g. of 2,6-dichloro-*p*-phenylenediamine dissolved in 20 ml. of dry pyridine was added a solution of 2.8 g. of benzoyl chloride in 15 ml. of dry pyridine. After 4 days the pyridine solution was poured into *ca.* 100 ml. of 1:1 hydrochloric acid. The product weighed 5.1 g. (91%). Two recrystallizations from ethanol-water gave white micro-needles, m.p. 185–186°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O: C, 55.53; H, 3.59; N, 9.97. Found: C, 55.36; H, 3.33; N, 10.09.

Infrared analysis indicated NH bands at 3445, 3345 and 3250 cm.<sup>-1</sup>; amide C=O at 1630 cm.<sup>-1</sup>; monosubstituted benzene at 689 and/or 704 cm.<sup>-1</sup>; NH deformation band at 1535 cm.<sup>-1</sup>; NH<sub>2</sub> deformation band at 1595 cm.<sup>-1</sup>.

**2,6-Dichloro-*p*-phenylene-4-benzamide-1-benzenesulfonamide.**—To a solution of 5.1 g. of N<sup>1</sup>-benzoyl-3,5-dichloro-*p*-phenylenediamine in 70 ml. of dry pyridine was added 3.2 g. of benzenesulfonyl chloride dissolved in 20 ml. of dry pyridine and the reaction was allowed to proceed at room temperature for 3 days. Upon pouring into *ca.* 200 ml. of 1:1 hydrochloric acid a cream-colored precipitate formed weighing 7.26 g. (95.5%). Two recrystallizations from ethanol-water gave white needles, m.p. 235.5–237°.

*Anal.* Calcd. for C<sub>19</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S: C, 54.17; H, 3.35; N, 6.65. Found: C, 54.15; H, 3.23; N, 6.72.

A melting point of a mixture of this compound and the *α*-2-dichloro-*p*-phenylenemonobenzamidemonobenzenesulfonamide showed no depression. Infrared analyses were identical.

***p*-Phenylenemonopivalamidemonobenzenesulfonamide.**—To a solution of 17.7 g. of N-benzenesulfonyl-*p*-phenylenediamine in 80 ml. of dry pyridine was added 8.6 g. of pivalyl chloride in 20 ml. of dry pyridine. The mixture was cooled under running tap water until the initial warming had subsided (*ca.* 3 min.) and allowed to stand at room temperature overnight. After 17 hours the reaction mixture was poured into 200 ml. of concentrated hydrochloric acid containing crushed ice. A pale orange precipitate formed which after filtration and drying in a vacuum desiccator over calcium chloride weighed 22.4 g. (94.5%). Three recrystallizations from ethanol-water after treatment with Darco gave white needles, m.p. 190–191.5°.

(7) O. N. Witt, *Ber.*, **8**, 145 (1875); N. L. Drake, *et al.*, *THIS JOURNAL*, **68**, 1602 (1946).

*Anal.* Calcd. for C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S: C, 61.42; H, 6.06; N, 8.43. Found: C, 61.30; H, 6.01; N, 8.38.

Infrared analysis indicated NH bands at 3365 and 3140 cm.<sup>-1</sup>; amide C=O at 1650 cm.<sup>-1</sup>; SO<sub>2</sub> bands at 1332 and 1165 cm.<sup>-1</sup>; monosubstituted benzene at 690 and/or 725 cm.<sup>-1</sup>; NH deformation band at 1525 cm.<sup>-1</sup>.

***α*-Chloro-*p*-phenylenemonopivalamidemonobenzenesulfonamide.**—A suspension of 3.3 g. of *p*-phenylenemonopivalamidemonobenzenesulfonamide and 4.4 g. of lead tetraacetate in 300 ml. of dry thiophene-free benzene was heated under reflux with stirring for 2 hours. The insoluble lead diacetate was removed by filtration. Dry hydrogen chloride was passed into the orange benzene filtrate for *ca.* 30 minutes. The resulting amber solution was concentrated to *ca.* 50 ml. and ethanol added to displace the benzene. The ethanolic solution (Darco) was filtered, concentrated to *ca.* 50 ml., water added to the cloud point and the solution allowed to stand overnight. An oil separated which was taken up in acetone, poured into water and allowed to stand several days. There was obtained a crude pink product which weighed 3.02 g. (83%). Three recrystallizations from methanol-water and one from acetone-water gave white needles, m.p. 164.5–166°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>16</sub>ClN<sub>2</sub>O<sub>2</sub>S: C, 55.65; H, 5.22; N, 7.64. Found: C, 55.88; H, 5.29; N, 7.41.

Infrared analysis indicated an NH band at 3260 cm.<sup>-1</sup>; amide C=O at 1655 cm.<sup>-1</sup>; SO<sub>2</sub> bands at 1337 and 1175 cm.<sup>-1</sup>; monosubstituted benzene at 685 and/or 721 cm.<sup>-1</sup>; NH deformation band at 1530 cm.<sup>-1</sup>.

**2-Chloro-*p*-phenylene-4-pivalamide-1-benzenesulfonamide.**—To 2.27 g. of N<sup>1</sup>-benzenesulfonyl-2-chloro-*p*-phenylenediamine dissolved in 10 ml. of dry pyridine was added 0.97 g. of pivalyl chloride dissolved in 5 ml. of dry pyridine. The mixture was cooled under running tap water for *ca.* 5 minutes with stirring and allowed to stand at room temperature. After 20 hours the pyridine solution was poured into 150 ml. of 1:1 hydrochloric acid to give a tan precipitate which, after filtration and air-drying, weighed 2.80 g. (95%). Two recrystallizations from methanol-water and one from acetone-water gave white needles, m.p. 164.5–166°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>16</sub>ClN<sub>2</sub>O<sub>2</sub>S: C, 55.65; H, 5.22; N, 7.64. Found: C, 55.71; H, 5.16; N, 7.46.

A melting point of a mixture of this product with *α*-chloro-*p*-phenylenemonopivalamidemonobenzenesulfonamide showed no depression. Infrared analyses were identical.

URBANA, ILLINOIS

## NOTES

### Derivatives of Quinoline-3-carboxylic Acid

By F. F. BLICKE AND J. E. GEARIEN

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Quinoline-3-carboxylic acid, was converted into its acid chloride hydrochloride and into *β*-diethylaminoethyl quinoline-3-carboxylate dihydrochloride and methobromide.

The acid chloride hydrochloride reacted with 2-aminopropanol and with 2-aminobutanol to form the 2-(1-hydroxy)-propyl- and the 2-(1-hydroxy)-butylamide of quinoline-3-carboxylic acid, respectively.

The 2-(1-hydroxy)-butylamide was tested for oxytocic activity in the Parke, Davis and Company laboratories; it was found to be inactive.

When ethyl quinoline-3-carboxylate was hydrogenated, in acetic acid-ethanol solution in the presence of platinum oxide catalyst, two atomic equiva-

lents of hydrogen were absorbed. Although no proof of structure was obtained, it was assumed that this product was ethyl dihydroquinoline-3-carboxylate, possibly the 1,4-dihydro derivative. This ester was hydrolyzed to the corresponding 3-carboxylic acid which seemed to decarboxylate readily, and the acid chloride could not be obtained.

The ethyl ester of the dihydro compound reacted with hydrazine hydrate to produce the acid hydrazide which, when treated with nitrous acid, yielded the acid azide. This substance reacted with ammonia to form dihydroquinoline-3-carboxamide.

#### Experimental

***β*-Diethylaminoethyl Quinoline-3-carboxylate Dihydrochloride and Methobromide.**—Quinoline-3-carboxylic acid<sup>1</sup>

(1) Prepared through 3-cyanoquinoline from 3-bromoquinoline. Cf. H. Gilman and S. M. Spatz, *THIS JOURNAL*, **63**, 1553 (1941), and Cl. Clairs and F. Collichonn, *Ber.*, **19**, 2763 (1886).

(20 g.) and 75 cc. of thionyl chloride were refluxed for 2 hours and the excess thionyl chloride was removed *in vacuo*. Benzene was added to the acid chloride hydrochloride and was then removed by distillation; this process was repeated several times. After the addition of 100 cc. of benzene, the mixture was cooled and 30 g. of  $\beta$ -diethylaminoethanol, dissolved in 50 cc., was added gradually. The mixture was refluxed for 6 hours, the precipitated diethylaminoethanol hydrochloride was removed by filtration and the solvent was distilled from the filtrate. The residue was washed with water, dissolved in ether, the solution was removed from the dried solution and the residue was distilled; b.p. 162–165° (1 mm.), yield 17 g. (54%).

The dihydrochloride precipitated when an ether solution of the ester was treated with hydrogen chloride; m.p. 193–195° after recrystallization from absolute ethanol.

*Anal.* Calcd. for  $C_{16}H_{20}O_2N_2Cl_2$ : N, 8.12; Cl, 20.54. Found: N, 8.13; Cl, 20.38.

After 12 hours, about one-half of the alcohol was distilled from a mixture of 2.7 g. of the ester base, 5 cc. of methyl bromide and 25 cc. of absolute ethanol. The methobromide precipitated after the addition of absolute ether; m.p. 177–179° after recrystallization from isopropyl alcohol; yield 2 g. (55%).

*Anal.* Calcd. for  $C_{17}H_{23}O_2N_2Br$ : N, 7.63; Br, 21.73. Found: N, 7.71; Br, 21.93.

**2-(1-Hydroxy)propylamide of Quinoline-3-carboxylic Acid.**—The acid chloride hydrochloride, obtained from 20 g. of quinoline-3-carboxylic acid, was suspended in 200 cc. of benzene and added, gradually, to a cooled solution of 35 g. of 2-aminopropanol<sup>2</sup> in 200 cc. of benzene. After 12 hours the benzene layer was decanted from the precipitated oil. The oil was washed with water and then allowed to remain under 100 cc. of 10% sodium carbonate solution for 2 hours. The solidified material was dissolved in alcohol, the solution was treated with charcoal, filtered and the product was precipitated by the addition of ether; yield 16 g. (59%), m.p. 110–112°.

*Anal.* Calcd. for  $C_{13}H_{14}O_2N_2$ : N, 12.17. Found: N, 12.29.

The base was dissolved in absolute ethanol and the solution was treated with hydrogen chloride. The hydrochloride precipitated after the addition of ether; m.p. 189–190° after recrystallization from absolute ethanol.

*Anal.* Calcd. for  $C_{13}H_{13}O_2N_2Cl$ : N, 10.51; Cl, 13.29. Found: N, 10.32; Cl, 13.42.

**2-(1-Hydroxy)butylamide of Quinoline-3-carboxylic Acid Hydrobromide.**—The base of this compound was prepared in the manner described above from the acid chloride hydrochloride, obtained from 15 g. of quinoline-3-carboxylic acid, mixed with 200 cc. of benzene and 31 g. of 2-aminobutanol<sup>3</sup> dissolved in 100 cc. of benzene. The crude product, which could not be purified by recrystallization, weighed 10 g. (48%). It was dissolved in the smallest possible amount of absolute ethanol and the solution was treated with hydrogen bromide. The salt precipitated after the addition of absolute ether; m.p. 165–167° after recrystallization from absolute ethanol.

*Anal.* Calcd. for  $C_{14}H_{17}O_2N_2Br$ : N, 8.62; Br, 24.58. Found: N, 8.51; Br, 24.48.

The hydrochloride proved to be hygroscopic.

**Ethyl Quinoline-3-carboxylate.**—The acid chloride hydrochloride, obtained from 10 g. of quinoline-3-carboxylic acid, was suspended in 20 cc. of benzene and added to 30 cc. of cooled absolute ethanol. The mixture was refluxed for 2 hours, the solvents were removed under reduced pressure, 10% sodium carbonate solution was added to the residue and the oily ester was extracted with ether. The solvent was removed from the dried solution; m.p. 68–69°<sup>4</sup> after recrystallization from petroleum ether (60–75°); yield 8 g. (68%).

**Ethyl Dihydroquinoline-3-carboxylate.**—Ethyl quinoline-3-carboxylate (12 g.), dissolved in a mixture of 25 cc. of acetic acid and 100 cc. of 95% ethanol, was hydrogenated under an initial pressure of 40 pounds in the presence of 0.2 g.

of platinum oxide catalyst. The solution rapidly absorbed 1.2 liters (0.05 mole) of hydrogen. Even after the addition of fresh catalyst, no further amount of hydrogen was absorbed. The mixture was filtered and the filtrate evaporated to dryness *in vacuo*. The residue was triturated with 10% sodium carbonate solution and the product was neutralized from isopropyl alcohol; m.p. 136–138°, yield 8 g. (66%).

*Anal.* Calcd. for  $C_{12}H_{13}O_2N$ : C, 70.91; H, 6.45; N, 6.88; mol. wt., 203. Found: C, 70.76; H, 6.25; N, 7.10; mol. wt., 207.

**Dihydroquinoline-3-carboxylic Acid.**—A mixture of 4 g. of the ester, 2 g. of potassium hydroxide and 25 cc. of 95% ethanol was refluxed for 4 hours. After removal of the alcohol, the residue was dissolved in water and the product was precipitated by the addition of acetic acid; m.p. 172° dec. after recrystallization from absolute ethanol; yield 3 g. (85%).

*Anal.* Calcd. for  $C_{10}H_9O_2N$ : N, 8.00. Found: N, 8.01.

**Dihydroquinoline-3-carboxamide.**—A mixture of 7.0 g. of ethyl dihydroquinoline-3-carboxylate, 25 cc. of 95% ethanol and 8.3 g. of an 85% aqueous solution of hydrazine hydrate was refluxed for 12 hours. After removal of the alcohol, the residue was triturated with 5 cc. of water and then was recrystallized from isopropyl alcohol; the hydrazide melted at 190–192°; yield 5.9 g. (89%).

The hydrazide (1.9 g.) was dissolved in a mixture of 10 cc. of acetic acid and 3 cc. of water, the solution was cooled to –5°, stirred and 0.76 g. of sodium nitrite was added in small portions. The solution was stirred for 15 minutes and during this time the yellow azide precipitated. It was filtered and washed free from acetic acid with ether. The azide decomposed rather violently at 134°; yield 1.6 g. (80%).

The azide (2 g.) was suspended in 250 cc. of ether and 5 cc. of 28% ammonia water was added. The mixture was stirred for 12 hours. The precipitated amide weighed 0.6 g. (42%); m.p. 180–182°.

*Anal.* Calcd. for  $C_{10}H_{10}ON_2$ : N, 16.02. Found: N, 15.84.

COLLEGE OF PHARMACY  
UNIVERSITY OF MICHIGAN  
ANN ARBOR, MICHIGAN

## Polarographic Study of Some Propylpyridonium Salts

BY EUGENE L. COLICHMAN<sup>1</sup> AND PATRICK A. O'DONOVAN<sup>2</sup>

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Pyridine, substituted pyridines, pyridine analogs, and many heterocyclic nitrogen compounds can be characterized and determined by polarography. This method most generally is applied to synthetic materials, but can often be adapted to naturally occurring products. A review article by Wawzonek<sup>3</sup> indicates the significance of the many polarographic investigations on heterocyclic nitrogen compounds. Pyridine and related amine materials are seen to give catalytic hydrogen waves which are attributed to the "onium" salts formed by hydrolysis.<sup>4,5</sup> Tompkins and Schmidt<sup>6</sup> have shown that "true" *one* electron reversible reduction waves

(1) North American Aviation, Inc., Atomic Energy Research Department, Box 309, Downey, California.

(2) Work described herein was from a thesis submitted by P. A. O'Donovan to the University of Portland in partial fulfillment of the requirements for the Degree of Master of Science.

(3) S. Wawzonek, *Anal. Chem.*, **21**, 61 (1949).

(4) E. Knobloch, *Collection Czechoslov. Chem. Commun.*, **12**, 407 (1947).

(5) P. C. Tompkins and C. L. A. Schmidt, *J. Biol. Chem.*, **143**, 643 (1942).

(6) P. C. Tompkins and C. L. A. Schmidt, *Univ. of Calif. Pub. Physiol.*, **8**, 221, 229, 237, 247 (1943).

(2) F. F. Blicke, J. A. Faust, R. J. Wazynski and J. E. Gearien, *THIS JOURNAL*, **67**, 205 (1945). A part of the material was obtained from the Carbide and Carbon Chemicals Corporation.

(3) Purchased from the Commercial Solvents Corporation.

(4) Reference 1, m. p. 69–69.5°.