leading to II, both 1,2- and 1,4-addition mechanisms were considered. It seems evident, however, that III could not be formed by 1,2-addition of aminopyridine to the quinone carbonyl groups. One can envision four possible structures for the initial reaction intermediate produced by 1,4-addition and attachment of either the ring nitrogen or the amino group to the carbon atom of II bearing either the chlorine or the oxygen function. Insomuch as Fieser has shown[6] that 2-ethoxy-3-chloro-1,4-naphthoquinone yields the 2-anilino-3-chloro compound when treated with aniline, structures IV and V appear more attractive for the initial intermediate than do the two alternative possibilities. The formation of III could then occur from either IV or V by the paths shown. Now VI and VII could, *a priori*, also be produced by the 1,4-addition of 2-aminopyridine to 2,3-dichloronaphthoquinone, and in Part I[1] it was remarked that if such were the case, it is curious that III was not produced instead of II. As III is produced in the present reactions, it seems probable that VI (or VII) is not an intermediate in the formation of II, and this lends weight to the probability that the reaction of 2-aminopyridine and 2,3-dichloronaphthoquinone occurs by a 1,2- and not a 1,4-addition mechanism.

While the foregoing may provide a useful working hypothesis, it is in no way a complete explanation of the problem. Left unexplained, for example, are the curious differences in the behavior of I (R = Cl, R′ = OH, OCH_3, or $OCOCH_3$) and 2-acetamino-3-chloro-1,4-naphthoquinone,[1] and the nonreactivity of I (R = OCH_3, R′ = $NHCOCH_3$, or R = R′ = SCH_3) with 2-aminopyridine.

EXPERIMENTAL[7]

6H,11H-Benzo[f]pyrido[a]benzimidazole-6,11-dione (III). A mixture of 2.36 g. of 2-ethoxy-3-chloro-1,4-naphthoquinone,[8] 2.00 g. of 2-aminopyridine, and 5 ml. of dry ethyleneglycol dimethyl ether ("Diglyme") was stirred and boiled under reflux for 20 hr., then was diluted with water and filtered. The dark solid (2.28 g.) was dissolved in acetic acid, diluted with water, refiltered, and washed well with water and methanol. Vacuum sublimation of this material, (weight 1.60 g.) gave 1.08 g. of yellow-brown needles. Crystallization from chlorobenzene gave 0.85 g. (34.3% yield) of golden-tan needles, m.p. 297–298°, λ_{max} 227, 242.5*, 248, 275, 298, 312, and 336 mμ (ϵ 17,450, 26,570, 34,140, 25,900, 15,450, 8,320, 3,735).

This same product was obtained by this procedure when the ethoxychloronaphthoquinone was replaced by either hydroxychloro- or acetoxychloronaphthoquinone.

Anal. Calcd. for $C_{15}H_8N_2O_2$: C, 72.57; H, 3.25; N, 11.29; O, 12.80. Found: C, 72.45; H, 3.41; N, 10.93; O, 12.80.

1,2,3,4-Tetrahydro-6H,11H-benzo[f]pyrido[a]benzimidazole-6,11-dione. Hydrogenation of I in ethanol over Adams catalyst, and air-oxidation of the resulting hydroquinone produced the tetrahydro compound, which crystallized from acetonitrile in yellow needles, m.p. 251–252°, having an infrared spectrum identical with that of the material prepared[2] by another route.

2-Aminopyridine salt of 2-chloro-3-hydroxy-1,4-naphthoquinone. A solution of 2.09 g. of 2-chloro-3-hydroxynaphthoquinone and 1.00 g. of 2-aminopyridine in 45 ml. of ethyl acetate was stirred and boiled for 0.25 hr., then cooled and filtered. The bright red solid weighed 2.84 g. (100% yield) and melted at 174–176°. A sample crystallized twice from acetonitrile formed brick red microcrystals, m.p. 178.4–179.4°.

Anal. Calcd. for $C_{15}H_{11}ClN_2O_3$: C, 59.50; H, 3.63; Cl, 11.72; N, 9.25; O, 15.85. Found: C, 59.48; H, 3.55; Cl, 11.71; N, 9.13; O, 16.00.

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(7) All melting-points were taken in Pyrex capillaries using a Hershberg melting-point apparatus and Anschütz thermometers.

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A Convenient Preparation of the 1-Methyl Betaines of Pyridine Carboxylic Acids

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The 1-methyl betaines of the various pyridine carboxylic acids have been prepared in many ways. For example, pyrolysis of methyl *iso*-nicotinate has afforded the 1-methyl betaine of isonicotinic acid[2] in fair yield. The various betaines have also been prepared by methylation of the acid with methyl iodide followed by treatment with silver oxide,[3] and by methylation with methyl sulfate followed by treatment with barium hydroxide.[4] Ion exchange columns have also been used. The methiodides of the three pyridine carboxylic acids were converted to the corresponding betaines by passing the solutions through a quaternary ammonium resin in the hydroxide form.[5]

These preparations suffer from several disadvantages. Those that use silver oxide invariably afford dark solutions and betaines that are difficult to purify. The use of strong base hydroxide exchange columns on the acid salts necessitates the use of very dilute solutions, for the heat of neutralization of the strong base with the acid salt liberates a considerable amount of heat. This latter

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problem is particularly serious for homarine, which is very temperature sensitive and decarboxylates readily, with the formation of dark solutions.

The best solution to the problem is to use a strong base ion-exchange resin to hydrolyse an ester rather than to neutralize the acid salts. The heating problem mentioned above is eliminated, as the saponification of the ester salt is not particularly exothermic. The procedure has the added advantage in that the ester methiodides can be easily purified by recrystallization before use, in contrast to the methiodides of the free acids which are difficult to separate from unreacted acid.

The eluate from passage of the ester methiodide through a strong base hydroxide column is neutral, colorless, and iodide free. Evaporation of the aqueous solutions using a rotary evaporator at room temperature readily affords the hydrated betaines in colorless crystalline form of high purity and in high yield.

EXPERIMENTAL[6]

1-Methyl betaine of isonicotinic acid. A solution of 5.00 g. (17.0 mmoles) of 1-methyl-4-carbomethoxy pyridinium iodide, m.p. 189–191° dec.,[7] in 50 ml. of water was passed through a 2 cm. × 15 cm. column of Dowex-1 in the hydroxide form. The column was eluted with 50 ml. of water and the neutral, colorless, iodide free eluate evaporated on a rotary evaporator at room temperature to a semisolid paste. To this was added 10 ml. of ethanol and the white solid filtered, giving 2.08 g., m.p. 286–289° (immediate decrepitation and loss of water when the sample was placed in the melting point apparatus, decomposition at the melting point). The addition of a few milliliters of ether to the mother liquor afforded an additional 0.28 g., m.p. 286–288°. Total yield 89.5%. Reported[2] m.p. 264° (anhydrous).

Anal. Calcd. for $C_7H_7O_2N \cdot H_2O$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.31; H, 5.63; N, 8.97.

Picrate of 1-methyl betaine of isonicotinic acid. To a solution of the betaine in alcohol was added a saturated alcoholic solution of picric acid, giving a yellow picrate, m.p. 214–216°; reported[4] m.p. 215–217°.

Anal. Calcd. for $C_{13}H_{10}O_9N_4$: C, 42.63; H, 2.75; N, 15.30. Found: C, 42.87; H, 2.74; N, 15.49.

Trigonelline. A solution of 5.00 g. (17.0 mmoles) of 1-methyl-3-carbomethoxy pyridinium iodide, m.p. 128–130° dec.[8] in 50 ml. of water was passed through a 2 cm. × 15 cm. column of Dowex-1 in the hydroxide form. The column was eluted with 50 ml. of water and the neutral, colorless, iodide free eluate evaporated on a rotary evaporator at room temperature to a semisolid paste. To the paste was added 10 ml. of ethanol and the white crystalline solid filtered off, giving 1.70 g., m.p. 230–233° (immediate decrepitation and loss of water when the sample was placed in the melting point apparatus, decomposition at the melting point). The addition of a few milliliters of ether to the mother liquor gave an additional 0.60 g., m.p. 230–233°. Total yield 87.4%. Reported[9] m.p. 218°.

Anal. Calcd. for $C_7H_7O_2NH_2O$: C, 54.19; H, 5.85; N, 9.03. Found: C, 53.80; H, 6.02; N, 9.01. Several analyses of the trigonelline hydrate were made by several microanalytical laboratories. The first two analyses were high in carbon by about 0.40%. The third sample was recrystallized from alcohol and was low in carbon by 0.39%, and is the one reported here.

Trigonelline picrate. To an alcoholic solution of trigonelline was added a saturated solution of picric acid in alcohol, giving a yellow picrate, m.p. 204–205°, reported[9] 205–206°.

Anal. Calcd. for $C_{13}H_{10}O_9N_4$: C, 42.63; H, 2.75; N, 15.30. Found: C, 42.76; H, 2.74; N, 15.52.

Homarine. A solution of 5.00 g. (17.0 mmoles) of 1-methyl-2-carbethoxy pyridinium iodide, m.p. 108–109,[8] in 50 ml. of water was passed through a 2 cm. × 18 cm. column of Dowex-1 in the hydroxide form and eluted with 50 ml. of water. The neutral, colorless, iodide free eluate was evaporated on a rotary evaporator at room temperature to a semisolid paste. To the paste was added 10 ml. of ethanol and the betaine filtered off to give 0.80 g. To half of the mother liquor was added a small amount of ether giving an additional 0.55 g., making the yield 58%. The material does not have a melting point, but slowly carbonizes when heated. Solutions of this betaine must not be heated or decomposition takes place.

Anal. Calcd. for $C_7H_7O_2N$: C, 61.31; H, 5.15; N, 10.21. Found: C, 61.31; H, 4.95; N, 9.98.

Homarine picrate. To the other half of the mother liquor mentioned above was added a saturated alcoholic picric acid solution to give an orange picrate, m.p. 158–160°, reported[4] 155–160°.

Anal. Calcd. for $C_{13}H_{10}O_9N_4$: C, 42.63; H, 2.75; N, 15.30; Found: C, 42.47; H, 2.84; N, 14.76.

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Preparation of Polyvinylamine Perchlorate[1]

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The synthesis of poly(vinylamine) and its derivatives has been detailed by Reynolds and Kenyon.[3] Since various other derivatives of poly(vinylamine) (V) were of interest as potential constituents of propellants, the synthesis of the polymer was under-

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(2) The authors are indebted to Dr. E. C. Horswill, Mr. P. McWain, and Mr. A. Reife for assistance in the early stages of this investigation.

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