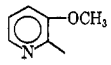
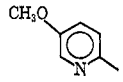
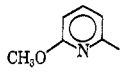
TABLE III

PHYSICAL AND SPECTRAL PROPERTIES OF KETONES, $RCOC_6H_5$

R =	Registry no.	Mp or bp, °C	Ir[a] (C=O), cm^{-1}	Nmr,[b] δ, ppm ($CDCl_3$ solvent)	Calcd for $C_{13}H_{11}NO_2$: C, 73.24; H, 5.17; N, 6.57
	19974-93-7	34–35, 174–175 (3 mm)	1660	3.8 (s, 3, OCH_3), 7.2–7.5 (m, 5, Ar), 7.6–7.8 (m, 2, Ar), 8.1 (m, 1, py)	C, 73.03; H, 4.97; N, 6.47
	29082-95-9	45–46	1640	3.9 (s, 3, OCH_3), 7.0 (m, 1, py), 7.3–7.6 (m, 4, Ar), 8.0–8.2 (m, 2, Ar), 8.5 (m, 1, py)	C, 73.62; H, 5.01; N, 6.42
	29082-96-0	75	1650	3.9 (s, 3, OCH_3), 7.2–7.6 (m, 4, Ar), 8.0–8.2 (m, 3, Ar), 8.4 (m, 1, py)	C, 72.94 H, 5.27; N, 6.22
	29082-97-1	124–127 (2 mm), 40–42	1640	3.9 (s, 3, OCH_3), 6.9 (m, 1, py), 7.3–7.8 (m, 8, Ar)	C, 73.04; H, 4.98; N, 6.32

[a] In $CHCl_3$, 2–6% solution. [b] Py = pyridine protons.

Experimental Section

All melting points are uncorrected and were obtained using the Fisher-Johns melting block. Infrared spectra were recorded with a Beckman IR-8 spectrometer. Nmr spectra were taken on a Varian Model A-60 spectrometer; chemical shifts are reported in parts per million (δ) from TMS as the internal standard. The mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E spectrometer at 70 eV and 200°. The properties of the carbinols and ketones are reported in Tables II and III. The general procedure for the Hammick reaction has already been described.

3-Methoxypyridine-2-carboxylic Acid.—A solution of 6.0 g (0.032 mol) of 2-bromo-3-methoxypyridine[8] in 50 ml of anhydrous ether was added to a solution of *n*-butyllithium (0.06 mol) in 50 ml of ether at −40 to −50° over a period of 30 min. The resulting red mixture was stirred for 15 min below −40° and then poured into a slurry of excess Dry Ice in 200 ml of ether. After standing overnight, the ethereal slurry was extracted with 50 ml of water. The aqueous extract was washed twice with 20 ml of benzene, the benzene extracts being discarded. The aqueous solution was made acidic (pH 4) by the addition of 48% hydrobromic acid solution. A saturated solution of copper sulfate was added. After cooling in an ice bath, the grey precipitate of the copper salt was removed by filtration and washed with two 5-ml portions of cold water. The copper salt was then suspended in 50 ml of water and copper sulfide was precipitated by bubbling hydrogen sulfide through the warm solution. After removal of copper sulfide by filtration, the filtrate was evaporated to dryness at room temperature. The crude acid (2.8 g) was recrystallized from methanol (1.8 g, 37%): mp 130° (rapid decomposition); nmr (DMSO-d_6) δ 3.85 (s, 3, OCH_3), 7.41–7.55 (m, 2, pyridine-4 and -5 protons), 8.18 (m, 1, pyridine-6 proton), and 11.4 ppm (broad, 1, COOH).

Anal. Calcd for $C_7H_7NO_3$: C, 54.92; H, 4.57; N, 9.15. Found: C, 54.61; H, 4.65; N, 8.96.

4-Methoxypyridine-2-carboxylic Acid.—To a solution of 3.2 g (0.14 g-atom) of sodium in 150 ml of methanol, 4-nitropyridine-2-carboxylic acid[8] (5.0 g, 0.030 mol) was added. The mixture was refluxed for 2 hr and the methanol was removed by distillation. The residue was treated with hydrochloric acid until pH 3 was attained. The methoxy acid (3.9 g, 85%) was obtained *via* the copper salt as colorless crystals: mp 204° dec; nmr (DMSO-d_6) δ 3.95 (s, 3, OCH_3), 7.3 (m, 2, pyridine protons), 8.1 (m, 1, pyridine proton), and 11.2 ppm (broad, 1, COOH).

Anal. Calcd for $C_7H_7NO_3$: C, 54.92; H, 4.57; N, 9.15. Found: C, 54.61; H, 4.51; N, 9.06.

5-Methoxypyridine-2-carboxylic Acid.—To a solution of 12.3 g (0.1 mol) of 5-methoxy-2-methylpyridine[9] in 350 ml of water, 70 g (0.44 mol) of potassium permanganate was added in ten portions over 3 hr. The mixture was vigorously stirred and maintained at 90–95°. The hot mixture was filtered and the filtrate was made acidic (pH 4) by addition of hydrochloric acid after cooling. The acid (7.2 g, 47%) was isolated *via* the copper salt: mp 167°; nmr ($CDCl_3$) δ 3.85 (s, 3, OCH_3), 7.4–7.9 (m, 2, pyridine protons), 8.3 (m, 1, pyridine protons), and 9.8 ppm (broad, 1, COOH).

Anal. Calcd for $C_7H_7NO_3$: C, 54.92; H, 4.57; N, 9.15. Found: C, 54.62; H, 4.49; N, 9.08.

6-Methoxypyridine-2-carboxylic Acid.—To a solution of 6 g (0.26 g-atom) of sodium in 150 ml of methanol, 11 g (0.054 mol) of 6-bromopyridine-2-carboxylic acid[10] (made by the oxidation of 6-bromo-2-methylpyridine[11] using potassium permanganate) was added. The mixture was refluxed for 6 hr and the methanol was removed by distillation. To the residue 100 ml of water was added and the aqueous solution was made acidic (pH 2) by hydrochloric acid. The methoxy acid was removed by filtration (7 g, 84%): mp 129–130°; nmr ($CDCl_3$) δ 4.0 (s, 3, OCH_3), 7.0 (m, 1, pyridine-4 proton), 7.8 (m, 2, pyridine protons), and 9.2 ppm (broad, 1, COOH).

Anal. Calcd for $C_7H_7NO_3$: C, 5.492; H, 4.57; N, 9.15. Found: C, 54.67; H, 4.44; N, 9.21.

Registry No.—Benzaldehyde, 100-52-7; 3-methoxypyridine-2-carboxylic acid, 16478-52-7; 4-methoxypyridine-2-carboxylic acid, 29082-91-5; 5-methoxypyridine-2-carboxylic acid, 29082-92-6; 6-methoxypyridine-2-carboxylic acid, 26893-73-2.

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(9) L. Marion and W. F. Cockburn, *ibid.*, **71**, 3403 (1949).
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Improved Preparation of 6-Methoxybenzoxazolinone[1]

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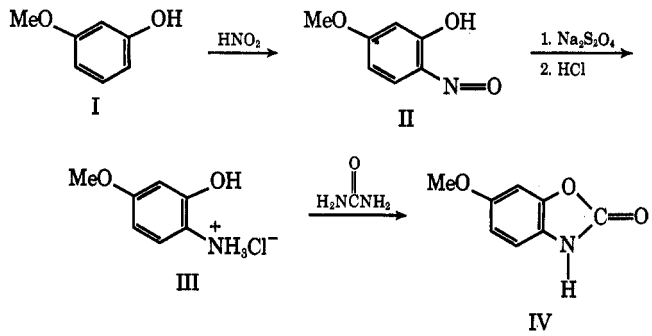
6-Methoxybenzoxazolinone (IV) has been implicated as a natural factor for the resistance of corn (*Zea mays L.*) to disease and insect attack.[2,3] To evaluate the role of IV as a disease resistance factor in Helmin-

(1) Mention of a trademark name, proprietary product, or specific equipment does not constitute a guarantee or warranty by the U. S. Department of Agriculture, and does not imply its approval to the exclusion of other products that may also be suitable.
(2) A. Stoessl in "Recent Advances in Phytochemistry," Vol. III, C. Steelink and V. C. Runeckles, Ed., Appleton-Century-Crofts, New York, N. Y., 1970.
(3) S. D. Beck, *Ann. Rev. Entomol.*, **10**, 207 (1965).

thosporium leaf blight of corn, we attempted to synthesize this compound according to reported methods.[4-6] These methods gave very low yields. One of the procedures was hazardous because phosgene was used.[5]

A shorter method with higher yield was developed. The first objective was to prepare the immediate precursor of IV, 2-amino-5-methoxyphenol hydrochloride (III), in high yield with a minimum number of steps. The orthoaminophenol obtained by reducing 2-nitroso-5-methoxyphenol (II) was not isolated. To



I II III IV

maximize the yield of III, neutralization of the reducing solution and other steps including the urea fusion were carried out in the dark or with photographic safety lights. Separatory funnels and flasks were flushed with N_2 gas. The uv, ir, melting point, and derivative data for IV were in good agreement with the literature values.[4-7]

Preparations of the amine hydrochloride which were black, blue, green, purple, or red reduced the yields of IV. Apparently some of the colored substances were partial oxidation products known as Wurster's salts.[8] Usually the white amine hydrochloride samples became grayish white and then blue. These blue preparations were fused with urea to yield about 17% IV when calculated on the basis of the initial starting material, *m*-methoxyphenol (I). This overall yield was about 60 times as great as the yield which we obtained by the use of the method of Klun and Brindley.[6]

Experimental Section[9]

2-Nitroso-5-methoxyphenol (II).—This compound was prepared in yields of 87–93% by the procedure of Hodgson and Clay.[10] The reaction mixture was held at 4° in the dark for 24 hr and the precipitate was isolated by filtration.

Preparation of 2-Amino-5-methoxyphenol Hydrochloride (III) for Fusion with Urea.—2-Nitroso-5-methoxyphenol (5.37 g) was suspended in 300 ml of water. Solid sodium hydrosulfite (18.5 g) was added slowly with continuous rapid stirring.[5,11] The reducing solution (bright yellow) was heated at 50–60° for 15 min, cooled, and neutralized to pH 6 with a saturated aqueous solution of $NaHCO_3$ added slowly by the drop with very rapid stirring. 2-Amino-5-methoxyphenol was extracted from the reducing solution (pH 6) with peroxide-free diethyl ether (eight 100-ml portions). The ether extract was passed through anhydrous Na_2SO_4. The 250-ml round-bottom flask containing the dry ethereal solution of the aminophenol was gently agitated and flushed with dry HCl gas for 1 min. The amine hydrochloride precipitated immediately as a white solid which became gray-white and then blue if water and O_2 were present. The ether was removed by rotatory evaporation *in vacuo* at 20°. The dry amine hydrochloride was mixed with urea (6 g) in a flask fitted with an air condenser, and heated in an oil bath at 170–180° for 2.5 hr.[4] Owing to its extreme instability, the orthoaminophenol was converted without delay to the hydrochloride. Highest yields were obtained when the amine hydrochloride was prepared and fused with urea as a continuous operation in the same flask in the absence of water.

Isolation of 6-Methoxybenzoxazolinone (IV) from the Fusion Mixture.—The fusion mixture was washed with 1.2 *N* HCl. The remaining residue was dissolved in ethyl alcohol, and about 50 ml of 1.2 *N* HCl was added. The alcohol was removed by rotatory evaporation *in vacuo* at 28°. The product (IV) was isolated from the acidic aqueous solutions by continuous extraction with diethyl ether. The wet ether was removed, and the residues were dissolved in a minimum amount of warm dry ether. The ethereal solution of crude IV was loaded on a silica gel (Adsorbosil-1) column which had been pressure packed in diethyl ether–petroleum ether (75:25 v/v) (EPE). The column was developed with EPE under low N_2 pressure and 5-ml fractions were collected (1 ml/min). IV was the first major compound to be eluted from the column and was detected in the fractions by thin layer chromatography on silica gel (microscope slides) developed with EPE (R_f 0.58). All compounds appeared as yellow spots on a purple background when the plates were sprayed with 3% aqueous $KMnO_4$. Fractions containing IV were combined and the solvent was removed. The light pink solid was decolorized with activated charcoal and recrystallized in water to give colorless needles: mp 154–155° (lit.[4] mp 154–155°); uv max (absolute EtOH) 231 mμ (ε 9138), 291 (5230); uv max (water) 230 mμ (ε 10,000), 286 (5380) [lit.[12] uv max (water) 230 mμ (ε 10,000), 287 (4500); lit.[5] uv max (water) 285–286 mμ (ε 5500)]; ir (KBr) 1326 (C—N stretching in Ar-NHR), 1498 (N—H bending, amide II band), 1620 (C=C aromatic skeletal in plane vibr), 1787 (C=O stretching, carbamate), 3330–3060 cm^{-1} (N—H stretching, multiple amide I band); mass spectrum (70 eV) *m/e* (rel intensity) M + 165.0428 (100%), calcd for $C_8H_7O_3N$ 165.0426. The ir and uv spectra were primarily the same as those reported in the literature.[6,7]

Anal. Calcd for $C_8H_7O_3N$: C, 58.18; H, 4.27; N, 8.48. Found: C, 57.96; H, 4.28; N, 8.42.

The benzimide was prepared: mp 165–167° (lit.[4] mp 163–164°); mass spectrum (70 eV) *m/e* (rel intensity) M + 269.0669 (14%), calcd for $C_{15}H_{11}O_4N$ 269.0688.

Registry No.—IV, 532-91-2.

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The Mechanism of Formation of Pentaazadecanetetraones in the Reaction of Aryl Isocyanates with *N*,*N*-Dimethylformamide

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The reaction of aryl isocyanates with *N*,*N*-dimethylformamide gives *N*-dimethyl-*N'*-arylformamidines[1]

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