the *m*- and *p*-vinyl groups have been calculated.

This investigation was undertaken in order to provide substituent constants (σ) for use in the Hammett equation[2] for the vinyl group. The large value of the reaction constant (ρ) for the dissociation of the substituted pyridinium ions[3] makes this system a good one in which to look for small effects. Accordingly the pK_a values of the following series of compounds were determined: pyridine, 2-vinylpyridine, 2-methyl-5-vinylpyridine, and 4-vinylpyridine. The 2-vinylpyridine was included to complete the series; the 2-methyl-5-vinylpyridine was used in place of the 3-vinylpyridine which is not commercially available.

Results and discussion. The pKa values and σ-values obtained are given in Table I. It is of interest to note that in the *meta* position the vinyl group exerts an electron withdrawing effect (σ positive) which may be attributed to an electron withdrawing inductive effect while in the *para* position the vinyl group exerts an electron releasing effect (σ negative) which may be attributed to an electron releasing resonance effect which is more powerful than the inductive effect from the *para* position. The 2-vinylpyridine has almost the same base strength as is calculated for the 3-vinylpyridine indicating that the increase in the inductive effect in going from the *meta* to the *ortho* position is approximately balanced by the resonance effect in the *ortho* position. The resonance which is possible in the pyridine system may cause the σ value for the *para* vinyl group to be more negative in the pyridine system than in other systems.

TABLE I

THERMODYNAMIC DISSOCIATION CONSTANTS OF THE VINYLPYRIDINES

	pK_a		
Compound	25°C.	Literature Values	$\sigma_{CH_2=CH}$[b]–
Pyridine	5.15	5.17,[c] 5.18,[d] 5.29[e]	
2-Vinylpyridine	4.92	4.92[f]	
3-Vinylpyridine[a]	4.87		+0.049
4-Vinylpyridine	5.62		−0.083
2-Methyl-5-vinylpyridine	5.67		

[a] Calculated on the basis of a contribution of +0.80 by the methyl group in 2-methyl-5-vinylpyridine. See H. C. Brown, D. H. McDaniel and O. Häfliger, "Dissociation Constants," in *Determination of Organic Structures by Physical Methods*, Edited by E. A. Braude and F. C. Nachod, Academic Press, New York (1955), p. 594 footnote a. [b] Calculated using a value of ρ of 5.685. See Ref. 3. [c] H. C. Brown and X. R. Mihm, *J. Am. Chem. Soc.*, **77**, 1723 (1955). [d] R. K. Murmann and F. Basolo, *J. Am. Chem. Soc.*, **77**, 3484 (1955). [e] Ref. 3. [f] H. E. Reich and R. Levine, *J. Am. Chem. Soc.*, **77**, 4913 (1955). See footnote 10.

EXPERIMENTAL

The vinylpyridines were obtained from the Reilly Tar and Chemical Corporation. They were purified by distilling under reduced pressure, preparing the picrates from the distillate and, after recrystallizing the picrates, hydrolyzing with dilute hydrochloric acid. The picric acid was extracted with benzene and the aqueous layer was then neutralized with dilute sodium hydroxide. The vinylpyridine was extracted with ether and the ether was evaporated under reduced pressure. The vinylpyridine was then rapidly distilled under vacuum and immediately solutions were made for the determination of pK_a. A 50 ml. sample of approximately $0.08M$ vinylpyridine was then titrated with $0.1N$ hydrochloric acid and the pH obtained during the course of the titration with a Beckman Industrial Model "M" pH meter. All determinations were carried out at room temperature (30°C. ± 1°C.). Values for pK' were obtained as the pH at the mid-point of the titration. Corrections for ionic strength were made using the Debye-Hückel equation and corrections for variation of the pK with temperature were made using the values given by Albert.[4] The thermodynamic pKa values at 25° are given in Table I. These values are about 0.05 unit lower than the pK' values.

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Synthesis of 7-Nitroindole

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Rydon and Siddappa[2] were unable to confirm the findings of earlier workers[3] reporting the Fischer cyclization of ethyl pyruvate *o*-nitrophenylhydrazone. Indole derivatives were not obtained in attempted ring closures with various acid catalysts under a variety of conditions; however, a material isomeric with the hydrazone was obtained under certain conditions. Since the analytical results reported by the earlier workers were unsatisfactory for both 7-nitroindolecarboxylic acid and 7-nitroindole, Rydon and Siddappa suggested that these compounds may not have been indoles and quoted a communication from the earlier workers who were in agreement with this conclusion.

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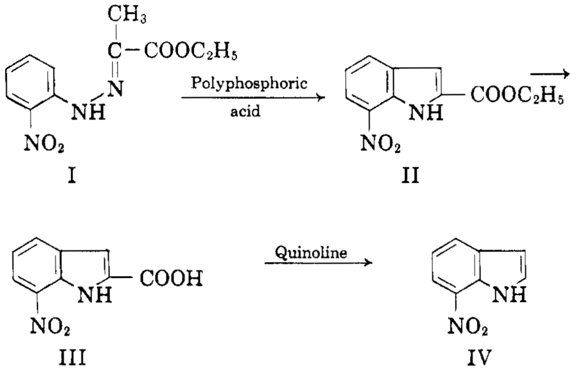
(1) Rosalie B. Hite, Post-doctoral Fellow, 1955–56. Present address: Department of Biochemistry, School of Medicine, University of Utah.

(2) H. N. Rydon, and S. Siddappa, *J. Chem. Soc.*, 2462 (1951).

(3) G. K. Hughes, F. Lions and E. Ritchie, *J. Proc. Roy. Soc. N. S. Wales*, **72**, 209 (1939); *Chem. Abstr.*, **33**, 6837 (1939).

During the course of some recent work with indolecarboxylic acids,[4,5] we also attempted ring closure of ethyl pyruvate *o*-nitrophenylhydrazone. In essence, results analogous to those of Rydon and Siddappa were obtained including the formation of a material isomeric with ethyl pyruvate *o*-nitrophenylhydrazone.

Recently Rydon and Tweddle[6] were successful in the cyclization of some substituted phenylhydrazones by means of polyphosphoric acid. We, therefore, re-investigated the ring closure of ethyl pyruvate *o*-nitrophenylhydrazone (I) with this reagent and were able to isolate ethyl 7-nitro-2-indolecarboxylate (II). Hydrolysis of this product gave 7-nitro-2-indolecarboxylic acid (III) which was decarboxylated to form 7-nitroindole (IV).



7-Nitroindole at a concentration of 100 γ per ml. inhibits the growth of *Lactobacillus arabinosus* 17–5. However, the growth inhibition is not reversed by anthranilic acid, indole, tryptophan or 7-indolecarboxylic acid.

EXPERIMENTAL[7]

Ethyl 7-nitro-2-indolecarboxylate. To 10 g. of polyphosphoric acid was added 2 g. of ethyl pyruvate *o*-nitrophenylhydrazone, and the mixture was stirred on a steam bath until it was homogeneous. The dark brown colored reaction mixture was then heated in an oil bath until a bath temperature of 195° was attained. The reaction mixture was allowed to remain at this temperature for 5 minutes and then removed from the oil bath. When the temperature of the mixture had decreased to 50°, 25 ml. of water was added and the mixture was heated on a steam bath. The solid material was broken by stirring and the suspension poured into a beaker. The remainder of the deep brown insoluble gum was stirred with an additional 25 ml. of water on the steam bath, and the aqueous mixture was combined with the first water suspension.

The water phase which contained a considerable amount of dark solid was extracted with three 50-ml. portions of ether The ether layer, orange colored, was washed with 5% sodium bicarbonate, with water, and finally dried over sodium sulfate. After drying, the ether was removed on a steam bath, and the residual oil was dissolved in 95% ethanol. To this solution, water was added until it became quite cloudy. This mixture was allowed to cool for several hours in a refrigerator. The yellow-orange needles separating were filtered and recrystallized from aqueous ethanol after treatment with charcoal. On cooling, lemon yellow needles were obtained. Yield of material melting at 92–93° was 250 mg. (13.4%).

Anal. Calc'd for $C_{11}H_{10}N_2O_4$: C, 56.41; H, 4.30; N, 11.96. Found: C, 56.50; H, 4.35; N, 11.95.

7-Nitro-2-indolecarboxylic acid. Ethyl 7-nitro 2-indolecarboxylate (100 mg.) was added to 10 ml. of a 10% aqueous solution of potassium hydroxide. The mixture was heated with stirring on a steam bath for several minutes. At the end of this time the deep red solution was filtered and allowed to cool. An equal volume of water was added to the mixture which was then vigorously shaken. This mixture was filtered and the filtrate was acidified with 6*N* hydrochloric acid. The cream-yellow solid was removed by filtration and recrystallized twice from aqueous ethanol. The very pale yellow needles were dried at 140° for 4 hours. Yield of material melting at 271–272° was 49.5 mg. (56%).

Anal. Calc'd for $C_9H_6N_2O_4$: C, 52.43; H, 2.93; N, 13.59. Found: C, 52.54; H, 3.24; N, 13.62.

7-Nitroindole. To 3 ml. of redistilled quinoline containing a trace of copper chromite was added 100 mg. of 2-carboxy-7-nitroindole. This mixture was heated in an oil bath at 205° for 2 hours with occasional stirring. At the end of this time, the hot black mixture was poured into a solution of 4 ml. of concentrated hydrochloric acid and ice. The mixture was filtered, and both the precipitate and the filtrate were extracted several times with ether. The ether extracts were combined and dried over sodium sulfate. Evaporation of the ether on a steam bath with subsequent cooling gave deep yellow needles. This material was recrystallized from aqueous ethanol. Yield of material melting at 95–96° was 39 mg. (49.5%); λ_{max} (95% ethanol): 232 mμ, 364 mμ; a plateau at 242–251 mμ with a slight maximum at 248–250 mμ; λ_{min}: 285 mμ. This solid when dissolved in Kovac reagent (Ehrlich reagent using isoamyl alcohol as solvent) gave a deep red color.

Anal. Calc'd for $C_8H_6N_2O_2$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.61; H, 4.03; N, 17.21.

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(7) All melting points are corrected; the authors are indebted to Dr. C. G. Skinner and Mr. J. Russell Claybrook for the microanalyses reported. The ultraviolet spectrum was determined on a Beckman Model DK-2 Recording Spectrophotometer.

Palladium Catalyzed Reduction of *p,p'*-Dihydroxybenzophenone

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Hydrogenation of *p,p'*-dihydroxybenzophenone (I) to *p,p'*-dihydroxydiphenylmethane(II) was carried out in excellent yield with palladium on carbon black. No report had previously been made on the use of a palladium catalyst in the reduction of a dihydroxybenzophenone. Bradlow and Van der