electrons. Structure (Ib), having no separation of charge, might be expected to contribute significantly to the resonance stability and thus favor the acidity of the methylene group.

For purposes of comparison we prepared the corresponding trimethylammonio derivative of pyruvic acid which cannot conjugate by expansion of the nitrogen valence shell. This derivative behaves as a monoprotic acid. Bordwell and Boutan[2] have reported a similar conjugative effect in *p*-dimethylsulfonio phenols.

Bromopyruvic acid and its methyl and ethyl esters react rapidly with dimethyl sulfide to give excellent yields of the corresponding dimethylsulfonio compounds. The reactions with the esters are best carried out without a solvent or a solvent in which the product is insoluble. Polar solvents such as alcohols are conducive to the formation of trimethylsulfonium bromide and alkyl methylmercaptopyruvates.[3]

Ethyl chloropyruvate reacts more slowly with dimethyl sulfide than the corresponding bromo compound and the reaction products are difficult to purify. Since chloropyruvic acid is difficult to prepare, dimethylsulfoniopyruvic acid chloride was obtained from the corresponding bromide.

EXPERIMENTAL

Bromopyruvic Acid. Triply distilled pyruvic acid[4] was brominated essentially in accordance with the procedure of Wegman and Dahn.[5] The crystalline mass was dissolved in the minimum volume of ether and diluted with petroleum ether to incipient turbidity. After several crystallizations pearly, white crystals were obtained, melting at 77–79°.[6] Bromopyruvic acid does not deteriorate when stored under petroleum ether in a refrigerator.

Dimethylsulfoniopyruvic acid bromide. To an ice cold solution of 8.35 g. (0.05 mole) bromopyruvic acid in 15 ml. of nitromethane was added 3.2 g. of dimethyl sulfide. On vigorous shaking a solid mass was formed. After standing overnight at room temperature the solid product was broken upon a sintered-glass filter and washed well with ether until it was reduced to a colorless powder. This was dissolved in a minimum volume of methanol and reprecipitated with ether, yielding 11.0 g. (95%) of crystals, m.p. 131–133°.

Anal. Calc'd for $C_5H_9BrO_3S$: Br, 34.92; neut. equiv., 114.5. Found: Br, 34.77; neut. equiv., 115.3.

Methyl bromopyruvate. Methyl pyruvate[7] was brominated according to the procedure of Archer and Pratt[8] for ethyl pyruvate. The compound was obtained in a 62–65% yield, b.p. 82–84° (10 mm.), n_D^{25} 1.4770, d_{20}^{25} 1.656, MRD: calculated 31.10, found, 30.96.

Anal. Calc'd for $C_4H_5BrO_3$: Br, 44.2. Found: Br, 44.4.

Ethyl dimethylsulfoniopyruvate bromide. Ethyl bromopyruvate,[8] 19.5 g. (0.1 mole) was added to 6.8 g. (0.11 mole) of dimethyl sulfide and cooled in an ice bath. After standing overnight, at room temperature, the solid cake was washed with acetone and then with ether until the crystals were no longer sticky. The crystals were dissolved in a minimum amount of cold methanol and precipitated with ether. The yield of product, melting at 88–90°, was 24.3 g., 95%.

Anal. Calc'd for $C_7H_{13}BrO_3S$: Br, 31.1; neut. equiv., 257. Found: Br, 31.2; neut. equiv., 261.

Repeated crystallizations of the sulfonio esters from polar solvents cause a gradual rise in melting point with a concomitant increase in the neutral equivalent due to the formation of $(CH_3)_3SBr$.

Methyl dimethylsulfoniopyruvate bromide. This compound was prepared in 85% yield by the procedure described for the analogous ethyl ester. M.p. 102–103°.

Anal. Calc'd for $C_6H_{11}BrO_3S$: Br, 32.9; neut. equiv., 243. Found: Br, 32.0; neut. equiv., 246.

Dimethylsulfoniopyruvic acid chloride. The chloride was prepared from the corresponding bromide by treatment with silver chloride in the usual manner. M.p. 140–141°.

Anal. Calc'd for $C_5H_9ClO_3S$: Cl, 19.23; neut. equiv., 184.5. Found: Cl, 19.28; neut. equiv., 186.

Trimethylammoniopyruvic acid bromide. Bromopyruvic acid, dissolved in methanol, was treated with excess trimethylamine. The precipitate formed on addition of ether was collected on a filter and washed with ethyl ether. The product was dissolved in absolute alcohol and acidified with hydrogen bromide. Addition of acetone precipitated trimethylammonium bromide. The filtrate from this mixture was diluted with ether and refrigerated overnight. The trimethylammoniopyruvic acid bromide which formed was collected on a filter and was recrystallized from an ethyl alcohol-ethyl ether mixture. M.p. 180–181° dec.

Anal. Calc'd for $C_6H_{12}BrNO_3$: Br, 35.4; neut. equiv., 226. Found: Br, 35.2; neut. equiv., 223.

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(2) F. G. Bordwell and Pierre J. Boutan, *J. Am. Chem. Soc.*, **78**, 87 (1956). This paper presents an excellent discussion, with pertinent references, on the conjugative effect of various sulfur groupings.

(3) Einar Biilmann and K. A. Jensen [*Bull. soc. chim. France*, **3**, 2310 (1936)] observed the same result with ethyl 2-bromopropionate and dimethyl sulfide. As in our case, the corresponding acid did not behave in this manner.

(4) V. E. Price and L. Levintow, *Biochemical preparations*, Eric G. Ball, Editor, John Wiley and Sons, Inc., New York, 1952, p. 22. For the instability of pyruvic acid in storage see C. M. Montgomery and J. L. Well, *Science*, **120**, 843 (1954).

(5) J. Wegman and H. Dahn, *Helv. Chim. Acta*, **29**, 415 (1946).

(6) D. B. Sprinson and E. Chargall [*J. Biol. Chem.*, **164**, 424 (1946)] report a melting point of 74°. Wegman and Dahn, ref. (5), give the melting point as 54–55°. Our product was analyzed for bromine, was converted to the 3,5-dinitrophenylhydrazone, m.p. 180°, and was condensed with benzamide to yield 2-phenyloxazole-4-carboxylic acid, m.p. 206–208°.

(7) A. Weissberger and C. J. Kebler, *Org. Syntheses*, Coll. Vol. **2**, 610 (1955).

(8) S. Archer and M. G. Prat, *J. Am. Chem. Soc.*, **66**, 1956 (1944).

Base Strength of Monovinylpyridines

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The base strengths have been determined for the monovinylpyridines and from these the σ values for

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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 $p\mathrm{K_a}$ 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 *p*Ka 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

	$p\mathrm{K_a}$		
Compound	25°C.	Literature Values	$\sigma_{\mathrm{CH_2{=}CH}^{b}-}$
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 $p\mathrm{K_a}$. A 50 ml. sample of approximately $0.08M$ vinylpyridine was then titrated with $0.1N$ hydrochloric acid and the *p*H obtained during the course of the titration with a Beckman Industrial Model "M" *p*H meter. All determinations were carried out at room temperature (30°C. ± 1°C.). Values for $p\mathrm{K}'$ were obtained as the *p*H at the mid-point of the titration. Corrections for ionic strength were made using the Debye-Hückel equation and corrections for variation of the *p*K with temperature were made using the values given by Albert.[4] The thermodynamic *p*Ka values at 25° are given in Table I. These values are about 0.05 unit lower than the $p\mathrm{K}'$ values.

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(2) (a) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII; (b) H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

(3) H. H. Jaffe and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 4441 (1955).

(4) A. Albert, *The Acridines, Their Preparation, Physical, Chemical and Biological Properties and Uses*, Edward Arnold and Co., London, 1951, p. 118.

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).