and 0.11 mole (5.5 g.) of hydrazine hydrate gave 31 g. of crude reaction product. The crude reaction product was mixed well with 46 g. of phosphorus pentasulfide and was then heated under an efficient reflux condenser for 1.5 hr. at 300°. There was obtained 18.8 g. (56% yield) of 2,5-bis-(pentafluoroethyl)-1,3,4-thiadiazole, b.p. 116–118°.

Anal. Calcd. for $C_6F_{10}N_2S$: C, 22.37; F, 58.98; N, 8.70; S, 9.96. Found: C, 22.62; F, 58.75; N, 8.26; S, 9.43.

The infrared spectrum showed absorptions at 6.83 μ (—C=N—), 6.90 μ, 7.45 μ, 8.25 μ (broad), 8.55 μ, 8.88 μ, 9.05 μ, 9.32 μ, 10.60 μ, 12.60 μ, and 13.35 μ.

2,5-Bis(4-hydrooctafluorobutyl)-1,2,4-thiadiazole (II. R_f = $H(CF_2)_4$—). A mixture of 10 mmoles (5.0 g.) of 1,2-bis-(5-hy-drooctafluorovaleryl)hydrazine and 23 mmoles (5 g.) of phosphorus pentasulfide was heated at a bath temperature of 250° for 1 hr. The volatile material was removed by distilla-tion. There was obtained 3.6 g. (74% yield) of 2,5-bis(4-hydrooctafluorobutyl)-1,3,4-thiadiazole, approximate b.p. 225°, m.p. 44.5–45.5°.

Anal. Calcd. for $C_{10}H_2F_{16}N_2S$: N, 5.76; S, 6.61. Found: N, 5.65; S, 6.44.

The infrared spectrum showed absorptions at 6.85 μ (—C=N—), 7.10 μ, 7.65 μ, 8.15 μ, 8.52 μ (broad), 8.94 μ, 9.85 μ, 11.55 μ, 11.22 μ, 11.30 μ, 12.37 μ, and 13.07 μ.

The fluorine magnetic resonance spectrum consisted of four chemically shifted resonances, a doublet having com-ponents at 4015 and 3965 c.p.s. (—CF_2H), and three singlets at 3495, 3170, and 2080 c.p.s. (internal —CF_x—). All the resonances exhibited considerable fine structure.

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Preparation and Absorption Spectra of 2-Methyl-4-vinyl- and 2-Methyl-6-vinylpyridine

G. B. GECHELE AND S. PIETRA

2-Methyl-4-vinyl- and 2-methyl-6-vinylpyridine were prepared by catalytic dehydrogenation of the corresponding ethyl derivatives. Ultraviolet and infrared spectra were reported and discussed.

2 - Methyl - 6 - vinylpyridine (2M6VP) and 2-methyl - 4 - vinylpyridine (2M4VP) were prepared with a view to comparing their properties, especially their absorption spectra, with other vinyl pyridines deriving, as by-products, from the preparation of 2-methyl-5-vinylpyridine through 2-methyl-5-ethyl-pyridine dehydrogenation.[1] 2-Methyl-4-vinylpyri-dine and 2-methyl-6-vinylpyridine were prepared by catalytic dehydrogenation of the corresponding ethyl derivatives.

Analyses and separations were performed by gas chromatography. The substances were identified by spectral analysis; molecular weight resulted from mass spectrometry determinations. The position of the substituent groups was determined by the identification of oxidation products (by paper chro-matographic analysis); it was also confirmed by the analysis of hydrogenation products.

2-Methyl-6-vinylpyridine had already been pre-pared[2] by reaction of formaldehyde on 2,6-lutidine.

Ultraviolet Spectra. 2-Methyl-6-vinylpyridine. Two bands are present in all solutions (methanol, hydro-chloric acid, sodium hydroxide). In the case of both methanolic and basic solutions, they are located at 282 mμ and 236 mμ (pH 10.02: ϵ_{282} 6570, ϵ_{236} 9450), while in the case of the acid solution, they lie at 292 mμ and 235 mμ (pH 3.35: ϵ_{292} 11400, ϵ_{235} 6280). As is already known,[3] these bands can be attributed to bathochromic shifts through conjugation of such

pyridine absorption as normally lies around 195 mμ (E band) and in the 250–260-mμ region (B band). The ultraviolet spectra of 2-methyl-6-vinylpyridine are reported in Fig. 1, in which the pH 3.35 and pH 10.02 absorption curves only are reported. The other measurements taken at pH 0.20 and pH 13.45, however, do not disclose the presence of an isosbestic point.
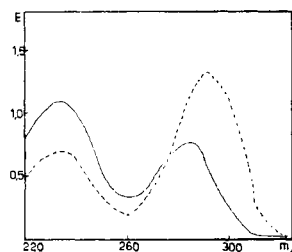

Fig. 1. Ultraviolet spectra of 2-methyl-6-vinylpyridine in acid (pH 3.35) (——) and base (pH 10.02) (-–) solutions (c, 0.12 mmole/l.). E denotes the optical density

2-Methyl-4-vinylpyridine. The basic and meth-anolic solutions show two bands at 281 and 242 mμ (pH 10.60: ϵ_{281} = 2910, ϵ_{242} 13,200). The acid solution, on the contrary, shows a broad absorption band only at 264 mμ (pH 3.35: ϵ_{264} 13,900). In our opinion, this probably arises from the lack of res-olution of two very near bands (type E and B,

(1) G. B. Gechele, A. Nenz, C. Garbuglio, and S. Pietra, *Chim. e Ind. (Milan)*, **42**, 959 (1960).

(2) J. Michalski and K. Studniazski, *Roczniki Chemii*, **29**, 1141 (1955).

(3) M. Swain, A. Eisner, C. F. Woodward, and B. A. Brice, *J. Am. Chem. Soc.*, **71**, 1341 (1949).

see above); indeed, while the E band shows a batho-chromic shift, the B band shifts in the opposite direction (hypsochromic).

B band behavior (hypsochromic shift in acid solutions and, in many cases, in methanol solutions also), while it would appear to be common to many γ-substituted pyridines, such as alkyl,[4] amino,[5] hydroxy,[6,7] etc., is the opposite to that observed in the case of α and β-substituted pyridines (e.g. see 2-methyl-6-vinylpyridine). The ultraviolet spectrum of 2-methyl-4-vinylpyridine is reported in Fig. 2. The pH 3.35 and pH 10.60 absorption curves are reported. The other readings were taken at pH 0.25, 1.32, 12.60, and 13.50.
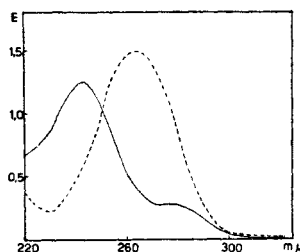

Fig. 2. Ultraviolet spectra of 2-methyl-4-vinylpyridine in acid (pH 3.35) (——) and base (pH 10.60) (–) solutions (c, 0.1 mmole/l.). E denotes the optical density

If we compare the λ_{max} of the ultraviolet absorption of the above substances with literature data for other vinylpyridines (see Table I), the following expression may be derived:

$$\lambda_{max} = 256 + 5\alpha + 21\alpha^* + 6\beta + 22\beta^* - 2\gamma + 20\gamma^*$$

TABLE I

ULTRAVIOLET ABSORPTION IN ETHANOL OR ALKALINE MEDIA

Compound	λ_{max}, mμ	Literature
Pyridine	256.5	—
2-Vinylpyridine	277.5	a
3-Vinylpyridine	278	b
4-Vinylpyridine	276	b
2-Methyl-5-vinylpyridine	285	b
2,5-Divinylpyridine	298	c
2-Ethyl-5-vinylpyridine	283	c
2-Vinyl-5-ethylpyridine	282	c
2-Methyl-6-vinylpyridine	282	—
2-Methyl-4-vinylpyridine	281	—
2,5-Diethylpyridine	267	c
2-Methyl-5-propylpyridine	268	c
2-Methyl-5-propen(1)ilpyridine	286	c
2-Methyl-5-isopropenilpyridine	285	c

[a] R. P. Mariella, L. F. A. Peterson, and R. C. Ferris, J. Am. Chem. Soc., 70, 1494 (1948). [b] S. Pietra and L. Lodi, communication before the Int. Meeting Mol. Spectroscopy, Bologna, 1959. [c] See ref. 1.

(4) R. J. L. Andon, J. D. Cox, and E. F. G. Herington, Trans. Far. Soc., 50, 918 (1954).

(5) E. A. Steck and G. W. Ewing, J. Am. Chem. Soc., 70, 3397 (1948).

where the coefficient α, β, and γ refer to the corresponding position in the pyridine nucleus, substituted by an n-alkyl group. The same coefficients, marked with an asterisk, refer to the same position substituted by a vinyl group. Coefficient value is zero when the corresponding position is not substituted, and one when it is substituted by the proper group. The above equation applies to alcoholic or alkaline solutions of the substituted pyridines. It is satisfactory for n-alkyl and or vinyl substituent groups, less satisfactory for propenyl groups or higher unsaturated homologs. It was derived from a combination of our data with Andon, Cox, and Herington's equation for n-alkyl groups.[4]

Infrared spectra (Figures 3 and 4). Low resolution of the instrument using a sodium chloride prism prevented the examination of the 3-μ region. It can only be remarked that the pattern in this area varies with the position of the substituting groups; this
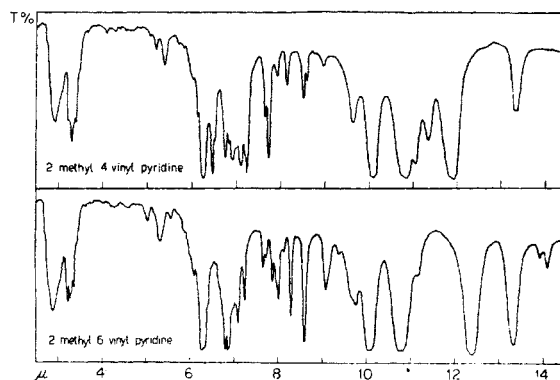

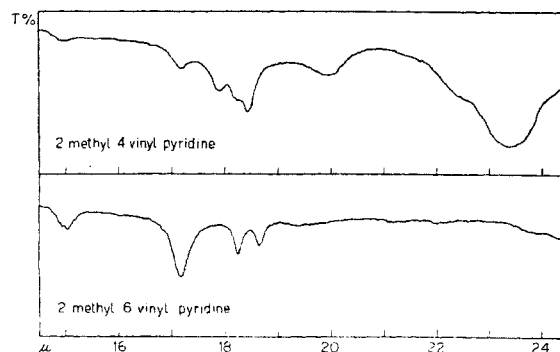Fig. 3. Infrared spectra in the sodium chloride region

Fig. 4. Infrared spectra in the potassium bromide region

depends on variation in the relative intensity of absorption caused by stretching vibration. It is impossible to detect the type of ring substitution from the shape of 2000–1700-cm.$^{-1}$ region, owing to the presence in this region of the vinyl harmonic (1860 cm.$^{-1}$ for 2-methyl-4-vinylpyridine and 1870 cm.$^{-1}$ for 2-methyl-6-vinylpyridine), as is the case in the known behavior of substances in this class. The

(6) G. W. Ewing and E. A. Steck, J. Am. Chem. Soc., 68, 2181 (1946).

(7) H. Specker and H. Gawrosch, Ber., 75, 1338 (1942).

region 1600–1400 cm.$^{-1}$ comprises the absorption of the ν (C=C) and ν (C=N) frequencies of the pyridine nucleus.

Some influence of electronic nature exerted by the substituents on frequencies and intensity is to be expected. Particularly, the substitution of a saturated carbon atom, which is attached directly to the ring, with an unsaturated one, gives rise to a frequency decrease in the higher frequencies[8]; this is shown in Table II.

TABLE II

ν (C=C) AND ν (C=N) STRETCHING VIBRATIONS OF PYRIDINE NUCLEUS[a]

Compound	Wave Numbers	Cm.$^{-1}$
2,4-Dimethylpyridine	1608	1563
2-Methyl-4-ethylpyridine	1610	1565
2-Methyl-4-vinylpyridine	1600	1548
2,6-Dimethylpyridine	1595	1580
2-Methyl-6-ethylpyridine	1600	1585
2-Methyl-6-vinylpyridine	1590	1575

[a] Our unpublished data.

The attribution for the remaining two vibrations of this type appears less certain; they probably occur at 1481 cm.$^{-1}$ and 1407 cm.$^{-1}$ for 2-methyl-4-vinylpyridine and at 1455 cm.$^{-1}$ and 1408 cm.$^{-1}$ for 2-methyl-6-vinylpyridine. The ν (C=C) absorption of the vinyl group also falls in this region, at 1630 cm.$^{-1}$ for 2-methyl-4-vinylpyridine and at 1635 cm.$^{-1}$ for 2-methyl-6-vinylpyridine; it is relatively weak in comparison with other vinylpyridines.

The 1380-cm.$^{-1}$ band is caused by methyl group deformation; the 1037-cm.$^{-1}$ absorption for 2-methyl-4-vinylpyridine and the 1025 cm.$^{-1}$ for 2-methyl-6-vinylpyridine are probably due to its rocking deformation. This behavior is similar to the one followed by aromatics when the methyl group is directly bonded to the ring.[9] The vinyl group gives rise to two vibrations with strong intensity, in the constant position near 990 cm.$^{-1}$ This last figure (out-of-plane deformation of —CH =CH$_2$) might appear abnormally high; however, it is common to all vinylpyridines. Both these vibrations can be used for identifying the presence of such a group in the pyridine bases. The characterization of the position of the substituting groups from the out-of-plane C—H ring deformation is more difficult; as a matter of fact, only small differences exist among the positions of these bands in the disubstituted pyridine bases.[10] These fall at 840 cm.$^{-1}$ and 748 cm.$^{-1}$ for 2-methyl-4-vinylpyridine and at 806 cm.$^{-1}$ and 749 cm.$^{-1}$ for 2-methyl-6-vinylpyridine. The lower frequencies are less intense.

It is very difficult to make any interpretation of the region between 650 cm.$^{-1}$ and 400 cm.$^{-1}$, because of the scanty knowledge we have of this region. In our opinion the vibration at 540 cm.$^{-1}$ and 430 cm.$^{-1}$ (2-methyl-4-vinylpyridine) and at 580 cm.$^{-1}$ 2-methyl-6-vinylpyridine might be attributed to ring deformation.

EXPERIMENTAL

2-Methyl-4-ethyl- and *2-methyl-6-ethylpyridine* were synthesized according to the method of Eckert and Loria[11] from ethyl iodide and α-picoline.

The reaction mixture, containing mainly α-picoline, 2-methyl-4-ethylpyridine, 2-methyl-6-ethylpyridine and 2-methyl-4,6-diethylpyridine, was subjected to fractional distillations with a 120-plates, heli-grid packed column, using a $^1/_{15}$ reflux ratio. Two main fractions were collected, I from 158.5°–159.5° and II from 176.4°–178.9°.

Chromatographic analysis (see Table III) disclosed that fraction I contained (%): water, 0.3; α-picoline, 1.2, 2-methyl-6-ethylpyridine, 95.3; 2,5-dimethylpyridine, 1.2; 2-methyl-5-ethylpyridine, 0.3, 2-methyl-4-ethylpyridine, 0.6; other impurities, 1. Fraction II contained (%): α-picoline, 0.1; 2-methyl-6-ethylpyridine, 3.0; 2-methyl-5-ethylpyridine, 1.5; 2-methyl-4-ethylpyridine, 93.4; other impurities, 2.0.

2-Methyl-6-ethylpyridine was identified by mass spectrometry molecular weight determination (calcd., 121; found, 121), by boiling point readings (b.p., 158–160°, lit.[12] b.p., 158–160°), and by picrate from methanol (m.p., 130°, lit.[12] m.p., 130–131°). 2-Methyl-4-ethylpyridine showed a mol. wt. of 121 (calcd., 121), b.p. 178° (lit.[13] b.p. 178°) and picrate (methanol), b.p., 141° (lit.[13] b.p., 140–142°).

Dehydrogenation. Fractions I and II were subjected separately to microdehydrogenation. A quartz tube, 0.28 sq. cm. section, was used; it was filled with catalyst (ferric oxide, chromium sesquioxide, and potassium oxide) 5.6 g., for a length of 20 cm.

The temperature of this zone was 600°. The mixture water/pyridine bases in the molar ratio 45/1 was introduced with a linear velocity of 2 m./sec., and a contact time of 0.1 sec. The reaction product was extracted with methylene chloride. After dehydration the solvent was evaporated in vacuum. The products were then separated by gas chromatography and subsequently analyzed.

Gas chromatography. A "Fractovap" apparatus (Carlo Erba, Milan) was used, with a column having a 6 mm. I.D. and 2 m. in length.

The filler was polyethylene glycol 400 (Carlo Erba, Milan) supported by "Celite C 22" (40–60 mesh) (Carlo Erba, Milan). The concentration of stationary phase was 28% by weight.

The temperature was 130°; transporting gas was hydrogen with a pressure (inlet) of 0.7 kg./sq.cm. The current in the detector was 30 ma. Chromatographic separations were performed under similar conditions, but with column of 20 mm. i.d. and 2–4 m. in length. One to 1.5 ml. of product was used in each separation.

In Table III the chromatographic retention volumes of the products described in this paper are reported.

2-Methyl-6-vinylpyridine. The chromatogram of fraction I, after dehydrogenation, showed approximately 40% of 2-methyl-6-ethylpyridine converted to 2-methyl-6-vinyl-

(8) A. R. Katritzky and J. N. Gardner, *J. Chem. Soc.*, 2198 (1958).

(9) R. R. Randle and D. H. Wiffen, *J. Chem. Soc.*, 3497 (1955).

(10) G. L. Cook and F. M. Church, *J. Phys. Chem.*, 61, 458 (1957).

(11) A. Eckert and S. Loria, *Monatsh.*, 38, 87 (1917).

(12) F. Runge, J. Freytag, and J. Kolbe, *Chem. Ber.*, 87, 873 (1954).

(13) H. L. Lochte and T. H. Cheavens, *J. Am. Chem. Soc.*, 79, 1667 (1957).

TABLE III

CHROMATOGRAPHIC RETENTION VOLUMES OF PYRIDINE BASES

Compound	Retention Volume[a]
α-Picoline	0.26
2-Methyl-6-ethylpyridine	0.35
2,5-Dimethylpyridine	0.44
2-Methyl-6-vinylpyridine	0.63
2-Methyl-5-ethylpyridine	0.69
2-Methyl-4-ethylpyridine	0.80
2-Methyl-5-vinylpyridine	1.00
2-Methyl-4-vinylpyridine	1.37

[a] Temp. = 130°; support = polyethylene glycol 400 (C. Erba, Milan), 28% on Celite.

pyridine, the other products being α-picoline, pyridine, etc.

2-Methyl-6-vinylpyridine was identified by molecular weight (mass spectrometry) (calcd., 119; found, 119), picrate (methanol, m.p., 160° (lit.[2] m.p., 160.5°) b.p., 72°/21 mm. (lit.[2] b.p., 73°/21 mm.).

2-Methyl-6-ethylpyridine was produced by hydrogenation in ethanol; the catalyst was palladium on carbon.

The infrared spectrum in the sodium chloride region coincides with the one already given in the literature.[14]

2-Methyl-4-vinylpyridine. From the chromatogram of the dehydrogenated fraction II, the peak with a 1.37 retention volume was identified as 2-methyl-4-vinylpyridine (conversion on 2-methyl-4-ethylpyridine, 40%). The product, separated with great purity from the chromatographic

column, formed a picrate (methanol) which melted at 166.5–167.5°, n_D^{20} 1.5410, and b.p. 76–77°/20 mm. Its molecular weight (mass spectrometry) is 119 (calcd. for C_8H_9N, 119).

Anal. Calcd. for C_8H_9N: N, 11.76. Found: N, 11.6.

The product, hydrogenated in ethanol, catalyst palladium on carbon, absorbed hydrogen, g. 1.65/100 g. (calcd. for C_8H_9N, 1.68), giving 2-methyl-4-ethylpyridine.

The permanganate oxidation gave 2,4-pyridinedicarboxylic acid, identified by paper chromatography.[15]

Infrared. Infrared spectra were determined with Perkin-Elmer model 21, from 2.5–15 μ with sodium chloride prism, and from 12–24.5 μ with potassium bromide prism; 0.05-mm. cells were used in both cases.

Spectra were measured immediately after the chromatographic separation. The 3450-cm.[-1] band is due to atmospheric moisture, which condensed on the walls of the Dry Ice–cooled trap, in which the chromatographic fractions were collected.

Ultraviolet. Spectra were determined from 350–220 mμ with a Spectracord Model 4000A, with 1-cm. silica cells.

The pyridine bases were examined in methanolic solutions, and in aqueous solutions of hydrochloric acid and sodium hydroxide at different pH values, in concentration of 0.12 mmole/l. (2-methyl-6-vinylpyridine) and 0.1 mmole/l. (2-methyl-4-vinylpyridine).

(14) *Sadtler Standard Spectra,* Midget Ed., 1959.
(15) F. Kufner and N. Faderl, *Monatsh,* **86**, 955 (1955).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, TEMPLE UNIVERSITY]

Further Preparation of Substituted 2,6-Bis(2'-pyridyl)pyridines[1]

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The preparation of some substituted terpyridines by the condensation of 2-acetylpyridine with aromatic aldehydes and ammonia is described. This procedure failed to provide the desired terpyridines when aliphatic aldehydes or acylpyridines other than acetyl were employed. A new route to unsubstituted 2,6-bis(2'-pyridyl)pyridine is described.

The effect of nuclear substituents upon the molecular extinction coefficient and oxidation potential of 1,10-phenanthroline- and 2,2'-bipyridine-iron(II) complexes has received considerable attention.[2] Analogous effects should be observable in the case of 2,6-bis(2'-pyridyl)pyridine-iron(II) complexes but preparative difficulties encountered in the terpyridine series have curtailed inquiry into this point.

2,6-Bis(2'-pyridyl)pyridine has been prepared by dehydrogenation of pyridine[3] and by coupling of bromopyridines.[4] Both these methods are of

limited applicability because of the rigorous conditions of reaction and the complexity of products. Frank and Riener[5] demonstrated that benzaldehyde and 2-acetylpyridine undergo cyclization with ammonia to provide 2,6-bis(2'-pyridyl)-4-phenylpyridine. This procedure (Method A, Experimental) was employed in previous work[6] to prepare a number of symmetrically substituted terpyridines. However, only benzaldehyde and 2-acetylpyridine bearing simple alkyl substituents were used. In order to study the scope of this reaction further, a number of variously substituted 2-acylpyridines was required. Their preparation was accomplished by converting the appropriate

(1) This work was supported by a grant (G 2162) from the National Science Foundation.
(2) W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Revs.,* **54**, 959 (1954).
(3) G. T. Morgan and F. H. Burstall, *J. Chem. Soc.,* 20 (1932).
(4) F. H. Burstall, *J. Chem. Soc.,* 1664 (1938).

(5) R. L. Frank and E. F. Riener, *J. Am. Chem. Soc.,* **72**, 4182 (1950).
(6) F. H. Case and T. J. Kasper, *J. Am. Chem. Soc.,* **78**, 5842 (1956).