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Nobuo Ikekawa* and Yoshihiro Sato**: Studies on the Coal Tar Bases. XI.[1] The Ultraviolet Absorption Spectra of Ethylpyridines.

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In a previous paper of this series,[2] the ultraviolet spectra of all methylpyridine isomers were reported. This paper gives data on the ultraviolet spectra in the 220~290 mμ region of three monoethylpyridines, 4-ethyl-2-methylpyridine, 2-ethyl-4-methylpyridine, 2-ethyl-6-methylpyridine, and 2,4-diethylpyridine.

Maximum peaks of the spectra in cyclohexane, 10% ethanol, and 0.2*N* sulfuric acid are shown in Table I. The spectra of ethylpyridines have more inflexions than that of methylpyridines and two or three maximum peaks appear in cyclohexane and ethanol. However, the bathochromic effect of the methyl group in α- or β-position in the pyridine ring and hypsochromic effect in γ-position are observed similarly in the case of ethyl group, and additive effect exists in these phenomena. Influence of a solvent in the spectra of ethylpyridines is also the same as in methylpyridines.

Table I. Ultraviolet Absorption Characteristics of Ethylpyridines

Pyridines	in cyclohexane		in 10% EtOH		in 0.2*N* H_2SO_4	
	λ_{max}(mμ)	ε_{max}	λ_{max}(mμ)	ε_{max}	λ_{max}(mμ)	ε_{max}
2-Ethyl-	256.5	2,550	257	3,150		
	261.5	2,550	262	3,620	263	6,900
	268	1,890	268.5	2,590		
3-Ethyl-	258	2,350	257.5	2,690		
	262~2.5	2,300	262.5	3,140	262.5	6,490
	268	1,760	269	2,230		
4-Ethyl-	255	1,680	255~5.5	2,260	252~2.5	4,220
			262~2.5	1,730		
2-Ethyl-4-methyl-	260	2,320	259.5	3,110	259~9.5	6,200
	267~7.5	1,880	266	2,550		
4-Ethyl-2-methyl-	260	2,140	259~9.5	2,990	259	5,820
	266.5	1,740				
2-Ethyl-6-methyl-	261	3,540				
	265.5	3,770	266.5	4,700	270~0.5	8,520
	273	2,970				
2,4-Diethyl-	260	2,040	259.5	2,970	259.5	5,280
			265.5	2,410		

Recently, Brown[3] reported the ultraviolet spectra of monoisopropyl- and mono-*tert*-butylpyridines. By the comparison of these values with our results, it may be concluded that introduction of other alkyl groups in place of the methyl group caused no effect on the maximum peak in the spectra of methylpyridines. Therefore, observation of the maximum peak of ultraviolet spectra in various solvents, as is the band of infrared spectra which is reported in the following paper,[4] is very helpful in determining the position of the alkyl group in the pyridine ring.

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Experimental

Material — 3-Ethyl-, 4-ethyl-, and 4-ethyl-2-methyl-pyridine were respectively prepared by the method of Fand,[5] Frank,[6] and Wawzonek.[7] 2-Ethyl- and 2,4-diethylpyridines were synthesized by the method of Ladenburg,[8] heating pyridine and EtI in a sealed tube at 280~300°. By the same method, 2-ethyl-6-methylpyridine was synthesized from α-picoline, and 2-ethyl-4-methylpyridine[9] from γ-picoline. The mixture of basic substances obtained from these procedures was fractionally distilled and the picrate of each fraction was recrystallized until constant melting point was obtained. The pure base was obtained from the picrate.

Method—The absorption spectra were determined with a Shimadzu Spectrophotometer type QB-50, with a quartz cell of 10 mm. optical depth, in the region of 220~290 mμ. Density measurements were never made at intervals of more than 2 mμ, while in the neighborhood of the maxima, the interval was decreased to 0.5 mμ. The concentration of the solutions varied from 0.2 m*M* to 0.05 m*M*. The temperature was at 20°±2°.

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Tsukasa Kuraishi : Synthesis of 4-Aminopyridazine.

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The synthesis of 4-aminopyridazine (I) has not yet been reported in literature. The writer obtained (I) quantitatively from 4-amino-3,6-dichloropyridazine by catalytic reduction, and comparison of the ultraviolet absorption spectra of 4-aminopyridazine and 3-aminopyridazine[1] is presented here.

Basskakow and Melnikow[2] obtained 1,2-dihydro-4-chloropyridazine-3,6-dione by heating chloromaleic anhydride with hydrazine sulfate in aqueous solution and Druey *et al.*[3] reported the absorption maxima of 3,4,6-trichloropyridazine. 4-Amino-3,6-dichloropyridazine (II) was obtained by heating 3,4,6-trichloropyridazine (III) with dehydrated ethanolic ammonia solution for 5 hours at 100~105°.

4-Aminopyridazine was obtained from the aminodichloropyridazine by reduction with palladium-charcoal as a catalyst.

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